

ence

EN FROM THIS ROOM

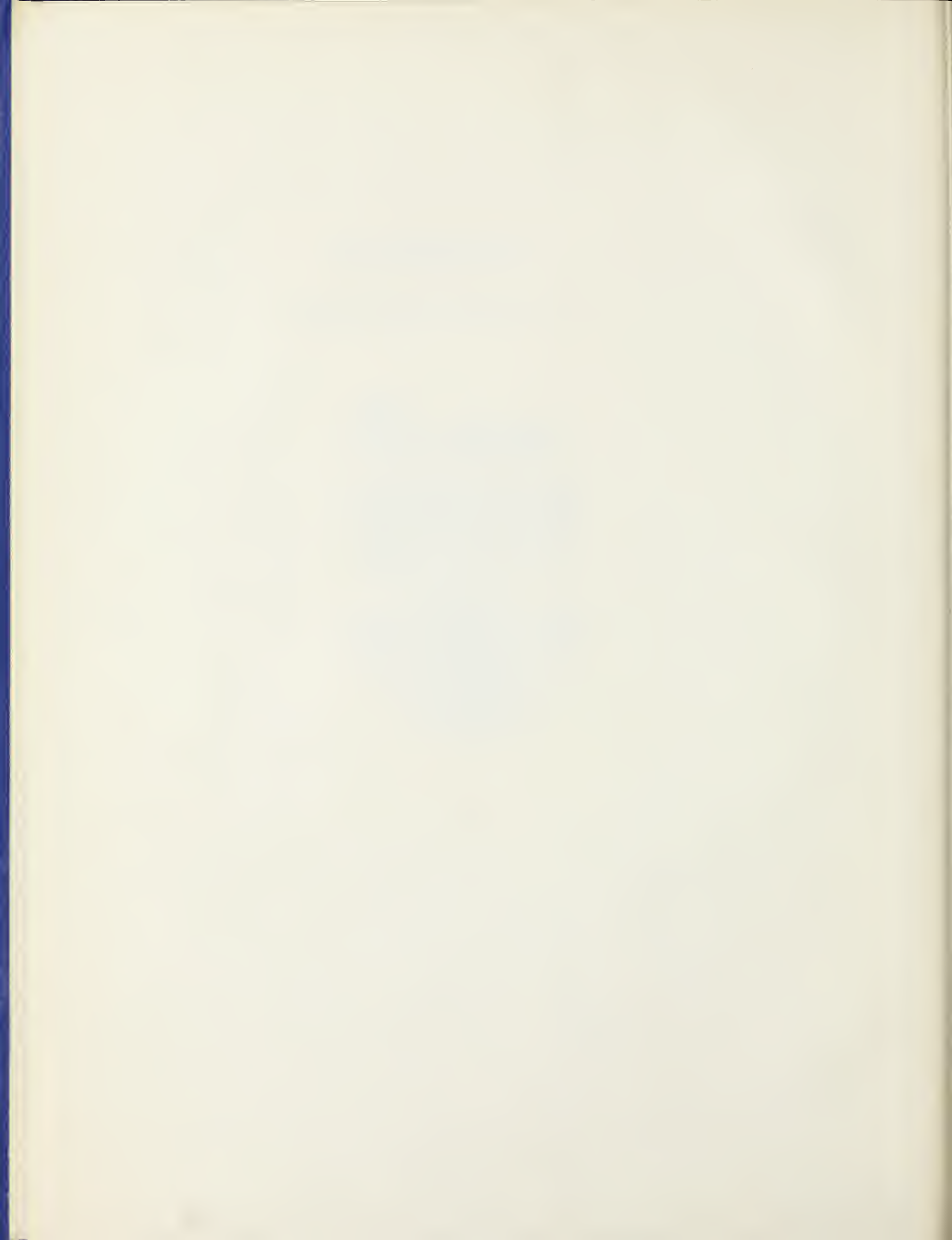
For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex LIBRIS
UNIVERSITATIS
ALBERTAENSIS









Digitized by the Internet Archive
in 2018 with funding from
University of Alberta Libraries

<https://archive.org/details/Paul1962>

Thesis
1962 (F)
56.

UNIVERSITY OF ALBERTA

GAUSSIAN FUNCTIONS IN MOLECULAR ORBITAL APPLICATIONS

by

REGINALD PAUL M. Sc.

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

September, 1962

CHAPTER INDEX

No.	Subject	Page
I	Introduction.....	1
II	General Methods	30
III	First Trial Function.....	48
IV	Second Trial Function.....	56
V	Third Trial Function	60
VI	Spectroscopic Constants	66

TABLE INDEX

No.	Title	Page
1	Results from the first trial function ; $R = 2$ a.u.	52
11	Results from the first trial function ; $R = 1.8$ and 2.2 a.u.	53
111	Results from the first trial function: three Gaussian combination	54
1V	Value of first function along internuclear axis	55
V	Results from the second trial function ; $R = 2$ a.u.	58
V1	Results from the second trial function: three Gaussian combination ..	59
V11	Results from third trial function: three Gaussian combination	63
V111	Value of third function along internuclear axis	64
1X	Comparison of energy at internuclear distance of 2 a.u.	65
X	Data used in calculation of spectroscopic constants	67
X1	Spectroscopic constants	67

FIGURE INDEX

No.	Title	Page
(1)	Generalized Flow Chart for Program used	46
(2)	Axial plot of wave function (three s-Gaussian combination, exact solution and Finkelstein-Horowitz curve)	68
(3)	Axial plot of wave function (two and three s-Gaussian combination)	69
(4)	Axial plot of wave function (two s and one p type combination along with the exact and Finkelstein-horowitz curves)	70

ABSTRACT

Since the availability of analytic solutions of the Schrodinger equation are limited to the most simple atoms and molecules, the necessity for methods of approximation has been keenly felt, one such method being the use of the linear variational method. However if this method is to be employed, use has to be made of an initial trial function, the form of which is somewhat arbitrary, and may depend upon any physical information available or chemical intuition. Because of their resemblance to the available analytic solutions, the Slater type functions have found extensive applications; but unfortunately the integrals involved are usually rather difficult to evaluate.

This work describes the use of Gaussian functions with which the evaluation of integrals is quite simplified. It was the purpose of this research to investigate the advantages and disadvantages of these functions with respect to the energy obtained, the electronic distribution and the derived results. For this purpose the hydrogen molecular ion was chosen as the testing ground mainly because of the availability of the exact solution and a number of theoretical approximations.

Three types of Gaussian function were used in the form of linear combinations, namely s type, p type and a form involving a weighting on the Z axis; the latter two were used with an idea of making the electronic distribution more favorable in the internuclear region. The functions mentioned above have been referred to in the text as the first, third and second trial

function. It was found that although the energies obtained from the first type of function, using a combination of three Gaussian functions (which is a number that can be readily handled by the IBM 1620) were quite good, the electronic distribution was very unfavorable chiefly because of the presence of rather flat maxima at the nuclei, as against the correct sharp appearance given by the exact solution. The form improves with a larger basis set; but a very large set involves a very laborious computation and renders the problem impracticable from the standpoint of time. In the second type of function there is a small decrease in the energy, whereas the numerical integration involved is too time consuming to permit a recommendation of this function for any practical use. In the third function, the introduction of a p type orbital, does in fact, cause an increase in the electron density in the middle region; but the expected improvements are largely offset by a rather poor representation of the s- character about the nuclei. This is caused by the small number of s type Gaussian functions used in order to keep the problem within practical limits.

It is concluded that it is advantageous from the practical point of view to introduce as the third basis function, one more s type member instead of a p type function.

In spite of the poor description of the electron distribution obtained by the Gaussians, the derived results such as the spectroscopic constants are quite good, casting doubt on the suggestion for their use as criteria for the "goodness" of a function.

ACKNOWLEDGEMENTS

Sincere thanks is extended to Dr. F. W. Birss for the suggestion of the topic and for the degree of patience shown towards me during my tenure here.

I would also like to thank my fellow graduate student Mr. W. G. Laidlaw for several interesting discussions and suggestions, and Mr. R. McClung for programming one of the Quadratic Minimizations.

I am indebted to the Computing Center of the University of Alberta for very kindly extending their facilities for the computation problems involved.

CHAPTER 1

INTRODUCTION

The hydrogen molecular ion has been the subject of a considerable amount of research, during the last couple of decades, mainly because it bears the same relation to most molecular problems, as does the hydrogen atom to most atomic problems; like the latter it is a single electronic species, free of interelectronic terms, and yet it has a distinctly molecular nature. It was decided therefore to use this ion as a testing ground for the use of the Gaussian Functions.

This molecule was discovered many years ago by J. J. Thomson in cathode rays, produced by the bombardment of ordinary hydrogen gas with electrons. Since then it has received a great deal of theoretical investigation, of which a short review would be worth while:-

Accurate solution of the Schrodinger equation:-

The system consists of

two nuclei, and one electron. From the Born - Oppenheimer approximation, one can neglect the motion of the nuclei, and write down the Schrodinger equation as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} \left(E + \frac{e^2}{r_A} + \frac{e^2}{r_B} \right) \psi = 0 \quad (1)$$

in which r_A and r_B represent the distance of the electron from nucleus A and B respectively. If elliptical co-ordinates ξ, η and φ defined by the equations

(2)

$$\xi = \frac{r_A + r_B}{r_{AB}}$$

$$\eta = \frac{r_A - r_B}{r_{AB}}$$

$$\varphi = \cos^{-1} \frac{x}{\sqrt{x^2 + y^2}}$$

(with r_{AB} as internuclear distance) be introduced, then the partial differential equation becomes separable into three total differential equations. Introducing:

$$\psi = \Sigma(\xi) H(\eta) \Phi(\varphi)$$

the equation reduces to:

$$\frac{d^2 \Phi}{d\varphi^2} = -m^2 \Phi \quad (2)$$

$$\frac{d}{d\xi} \left[(\xi^2 - 1) \frac{d\Sigma}{d\xi} \right] + \left(-\lambda \xi^2 + 2D\xi - \frac{m^2}{\xi^2 - 1} + \mu \right) \Sigma = 0 \quad (3)$$

with

$$1 \leq \xi \leq \infty$$

$$\frac{d}{d\eta} \left[(1 - \eta^2) \frac{dH}{d\eta} \right] + \left(\lambda \eta^2 - \frac{m^2}{1 - \eta^2} - \mu \right) H = 0 \quad (4)$$

with

$$-1 \leq \eta \leq +1$$

in which

$$\lambda = - \frac{2\pi^2 m r_{AB}^2 E}{h^2} \quad (4a)$$

(3)

$$D = \frac{g_{AB}}{a_0} \quad (4b)$$

Where m , λ and μ are undetermined parameters. The familiar

ψ equation possesses acceptable solutions for $m = 0, \pm 1, \pm 2, \dots$.

The subsequent procedure of solution consists of finding the

relation which must exist between λ and μ in order that the η equation posses a satisfactory solution, and then using this relation,

for finding from the ζ equation, characteristic values of λ .

This procedure was carried out by Burrau ⁽¹⁾ on the normal state of the hydrogen molecular ion, by a numerical integration of equations (3) and (4). More accurate studies have been made on equation (4) by Hyelleras ⁽²⁾ and on equation (3) by Jaffe ⁽³⁾ and Chakravarty ⁽⁴⁾.

From the definition of $\eta = \cos \vartheta$, it is evident that the only values this variable can take up, lie between -1 and +1, which also happens to be the limits of the associated Legendre function $P_l^{(m)}(\cos \vartheta)$, hence taking advantage of the complete nature of these functions one can write.

$$H(\eta) = \sum_{l=m}^{\infty} C_l P_l^{(m)}(\eta)$$

Substitution of this into equation (4) and simplification with the aid of the differential equation, satisfied by the associated Legendre function, one obtains

$$\sum_{\ell=|m|}^{\infty} c_{\ell} \{ \lambda \eta^2 - \mu - \ell(\ell+1) \} P_{\ell}^{(m)}(\eta) = 0 \quad (5)$$

Eliminating the factor η^2 by successive use of the ordinary recursion formula (5), and upon introducing the result so obtained into equation (5) a simple series in the functions $P_{\ell}^{(m)}(\eta)$ with coefficients independent of η results. Because of the orthogonality of these functions, their coefficients must vanish independently, in order that the series vanish. This gives the condition

$$\frac{(\ell-|m|-1)(\ell-|m|)}{(2\ell-3)(2\ell-1)} \lambda c_{\ell-2} + \left[\left\{ \frac{(\ell-|m|+1)(\ell+|m|+1)}{\ell(\ell+1)(2\ell+3)} + \frac{(\ell-|m|)(\ell+|m|)}{(2\ell-1)(2\ell+1)} \right\} \lambda - \mu - \ell(\ell+1) \right] c_{\ell} + \frac{(\ell+|m|+2)(\ell+|m|+1)}{(2\ell+3)(2\ell+5)} \lambda c_{\ell+2} = 0 \quad (6)$$

The equation (6) may now be considered, as a set of homogenous equations in the unknown quantity c_{ℓ} , with different values of ℓ . In order that this set may possess a non-trivial solution, the determinant must vanish. This gives then a determinantal equation involving λ and μ , from which one can determine the relation between them.

For the normal state of the system, with $m=0$ and ℓ even, the determinantal equation reduces to

(5)

$$\begin{pmatrix} \frac{1}{3}\lambda - \mu & \frac{2}{15}\lambda & 0 & 0 & \dots \\ \frac{2}{3}\lambda & \frac{11}{21}\lambda - 6\mu & \frac{4}{21}\lambda & 0 & \dots \\ 0 & \frac{12}{25}\lambda & \frac{24}{17}\lambda - 20\mu & 0 & \dots \\ 0 & 0 & 0 & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} = 0$$

Hyellerass carried out the solution of this equation, obtaining

$$\mu = \frac{1}{3}\lambda + \frac{2}{135}\lambda^2 + \frac{4}{8505}\lambda^3 - 0.000013\lambda^4 - 0.000006\lambda^5 \quad (7)$$

This gives the functional relation between the separation constant μ , and λ as derived from the η equation, the next step would be to do the same with the ξ equation and then equate them. The latter relation has been derived both by Jaffe and by Chakravarty.

If in equation (3) $2D$ is replaced by B , and μ by $-A$, the equation can be readily rearranged as

$$\frac{\partial}{\partial \xi} \left\{ (\xi^2 - 1) \frac{\partial \Sigma}{\partial \xi} \right\} - \frac{m^2 \Sigma}{\xi^2 - 1} + \left[-\lambda \xi^2 + B \xi - A \right] \Sigma = 0$$

setting

$$\Sigma = e^{-\sqrt{\lambda} \xi} (\xi^2 - 1)^{m/2} y \quad \text{and} \quad \lambda = \frac{\xi^2 - 1}{\xi + 1} \quad (8)$$

and taking $(1-x)^{p/2}$ for y one obtains after simplification

$$\begin{aligned} & \lambda(1-x)^p \frac{\partial^2 \Sigma}{\partial x^2} - \left\{ 2(p+1)\lambda(1-x) - (m+1)(1-x^2) + 4\sqrt{\lambda}x \right\} \frac{\partial \Sigma}{\partial x} + \left[\xi\sqrt{\lambda} + \frac{1}{2}B \right. \\ & \left. - \sqrt{\lambda}(m+1) \right] \frac{4x}{1-x} + p(p+1)x - (m+1)p(1+x) + m(m+1) - A - \lambda + B - \\ & 2\sqrt{\lambda}(m+1) \Sigma = 0 \end{aligned}$$

(6)

Taking ρ (which is as yet undefined) to be equal to

$m+1 - B/\sqrt{\lambda}$ the equation can be further simplified

$$x(1-x)^2 \frac{\partial^2 z}{\partial x^2} - \left\{ (m-2\rho-1)x^2 + (2\sqrt{\lambda} + \rho+1)2x - (m+1) \right\} \frac{\partial z}{\partial x}$$

$$+ \left\{ \rho(\rho-m)x \right\} - K \} = 0 \quad (9)$$

where

$$K = A + \lambda + (1-\rho)(m+1+2\sqrt{\lambda}) + 2m\sqrt{\lambda}$$

$$\rho = B/2\sqrt{\lambda}$$

The equation (9) is then an ordinary differential equation that can be solved by series integration, by setting

$$z = \sum_{n=0}^{\infty} a_n x^n$$

From whence one gets the recursion formula

$$f_{n-1} a_{n-1} + g_n a_n + h_{n+1} a_{n+1} = 0 \quad (10)$$

where

$$f_{n-1} = (n-\rho)(n+m+\rho)$$

$$g_n = -\left\{ 2n(n+2\sqrt{\lambda} + m+1-\rho) + K \right\}$$

$$h_{n+1} = (n+1)(n+m+1)$$

From (10) then

$$h_{n+1} \frac{a_{n+1}}{a_n} = -g_n - f_{n-1} \frac{a_{n-1}}{a_n}$$

$$= -g_n + \frac{h_n f_{n-1}}{g_{n-1}} \frac{h_{n-1} f_{n-2}}{g_{n-2}} (-1)^{n-1} \frac{h_1 f_0}{g_0} \quad (11)$$

But

$$\begin{aligned} f_{n+1} \frac{a_{n+1}}{a_n} &= -g_n - h_{n+1} \frac{a_{n+1}}{a_n} \\ &= -g_n - \frac{h_{n+1} f_n}{g_{n+1}} \frac{h_{n+2} f_{n+1}}{g_{n+2}} \end{aligned}$$

Again

$$f_{n+1} \frac{a_{n+1}}{a_n} + g_n + h_{n+1} \frac{a_{n+1}}{a_n} = 0$$

$$\therefore g_n - L_{n+1} - H_{n+1} = 0 \quad (12)$$

Where

$$L_{n+1} = \frac{h_{n+1} f_n}{g_{n+1}} \frac{h_{n+2} f_{n+1}}{g_{n+2}}$$

$$H_{n+1} = \frac{h_n f_{n-1}}{g_{n-1}} \frac{h_{n-1} f_{n-2}}{g_{n-2}} (-1)^n \frac{h_1 f_0}{g_0}$$

Hence from (12) as a first approximation one has

$$g_n = 0 \quad (13)$$

and to a second approximation, considering only the first convergents one has

$$g_{n+1} - \frac{h_{n+1} f_n}{g_{n+1}} - \frac{h_n f_{n-1}}{g_{n-1}} = 0 \quad (13a)$$

From (13) then

$$\left. \begin{aligned} K &= -2n(n+2\sqrt{\lambda}+m+1-p), \\ A &= -2n(n+2\sqrt{\lambda}+m+1-p)-\lambda-(1-p)(m+1+2\sqrt{\lambda})-2m\sqrt{\lambda} \end{aligned} \right\} \quad (14)$$

Hence substituting for K its value as given by (14) wherever it

(8)

occurs in the second order terms in (13a) ie in $\frac{h_{n+1}f_n}{g_{n+1}}$ and

$$\frac{h_n f_{n-1}}{g_{n-1}} \quad \text{one obtains on simplification}$$

$$-H = A = -2n(2+2\sqrt{\lambda}+m+1-p) - \lambda(1-p)(m+1+2\sqrt{\lambda}) - 2m\sqrt{\lambda} + \left[\frac{(n+1)(n+m+1)(n+1-p)(n+m+1-p)}{2(2n+2\sqrt{\lambda}+m+2-p)} - \frac{n(n+m)(n-p)(n+m-p)}{2(2n+2\sqrt{\lambda}+m-p)} \right] \quad (15)$$

This equation can be simplified for the ground state and equated to (7) obtained for the η part; with the help of these, one then proceeds to obtain the roots of λ from the definition of which, equation (4a), and by taking suitable values of λ_{AB} one can readily evaluate the E eigenvalue, which agrees remarkably well with experimental values.

The eigenfunction is given by

$$\psi = N \Sigma(\xi) H(\eta) \Phi(\varphi)$$

where N is the normalization constant.

$$\Sigma(\xi) = e^{-\sqrt{\lambda}\xi} (\xi^2-1)^{m/2} (1-x)^{p/2}$$

$$p = m+1 - \frac{B}{2\sqrt{\lambda}}, \quad x = \frac{\xi-1}{\xi+1} \quad \text{and} \quad z = \sum a_n \lambda^n$$

where the coefficients $a_n, a_{n+1}, a_{n+2}, \dots$ are connected by the recursion relation (10)

$$H(\eta) = \sum_{l=m}^{\infty} (c_l p_l^{(m)}(\eta))$$

the coefficients C_1, C_{1-1}, C_{1+1} are connected by the recursion relation (6) and

$$\Phi = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$$

However, the wave function obtained above is rather cumbersome, and difficult to handle, and it would be desirable to have an approximate treatment of the molecule.

Morse and Stueckelberg's degenerate perturbation treatment:-

One of the earlier attempts to study the hydrogen molecular ion by an approximation method was made by Morse and Stueckelberg in 1929⁽⁶⁾ using the perturbation method. These workers took advantage of the fact, that at least under two conditions, the eigenvalues and eigenfunctions of this species are known precisely (1) when the internuclear distance is zero, one gets the He^+ ion, which has exactly the same solutions as an hydrogen atom carrying a nuclear charge two, and (2) when the internuclear distance is infinity, one gets essentially an hydrogen atom and a proton at an infinite distance apart, the eigenfunctions and eigenvalues of the of the hydrogen atom are of course well known. In between these two extremes, there lies the hydrogen molecular ion being investigated.

The change over from the He^+ ion at a zero nuclear separation to an hydrogen atom and a proton at infinite nuclear separation via the H_2^+ lying in between, was considered by Morse and Stueckelberg in the light of the best co-ordinate system, that can be used to describe a particular species encountered, eg. an He^+ ion is best described in a spherical co-ordinate system, while an hydrogen atom with a proton at an infinite distance from it, would on the other hand be best described in parabolic co-ordinates, and in between the

hydrogen molecular ion is best suited for an elliptical system.

Since at a finite distance from the nucleus, each quantum number corresponds to a node, use can be made of the latter to keep track of the former during this process of changing internuclear distances.

Starting then from the He^+ ion, which might also be called the united atom, one has the spherical axes, r, θ and φ , with the corresponding quantum numbers n_r, n_θ and n_φ .

In the modern system of nomenclature

$$n = n_r + l + 1$$

$$l = n_\theta + n_\varphi$$

$$m = n_\varphi$$

$$n = (n_r + n_\theta + n_\varphi + 1)$$

or in other words the total quantum number is equal to the total number of nodes plus one. The energy is given by

$$E = -\frac{2\pi^2 m e^4}{h^2} \frac{Z^2}{n^2} = R \frac{Z^2}{n^2} = \frac{4R}{(n_r + n_\theta + n_\varphi + 1)^2}$$

where R is the energy of the hydrogen atom. The wave function here is the hydrogenic wave function with $Z=2$. Now suppose the internuclear distance is increased from zero to a finite value of r_{AB} , producing thereby an H_2^+ ion. One has in effect moved from a spherical system to an elliptical system, and use can be made of the corresponding co-ordinate system defined earlier. By taking limits of these co-ordinates one finds:

$$\lim_{r_{AB} \rightarrow 0} \xi = 2r/r_{AB}$$

$$\lim_{r_{AB} \rightarrow 0} \eta = \cos \theta$$

$$\lim_{r_{AB} \rightarrow 0} \varphi = \varphi$$

It is possible then to write

$$n_x \rightarrow n_\xi$$

$$n_\theta \rightarrow n_\eta$$

$$n_\varphi \rightarrow n_\varphi$$

and the total quantum number is still

$$n = (n_\xi + n_\eta + n_\varphi + 1)$$

But of course there is no energy expression available.

When the nuclei are moved still further apart to infinity, one ends up with a hydrogen atom at A, proton at B, or a proton at A and a hydrogen atom at B. The wave function describing this system will be a linear combination of these two forms, i.e.

$$\psi = \frac{1}{\sqrt{2}} (\psi_A \pm \psi_B)$$

where both plus and minus signs have to be taken, since the probability is given by the integral of $\psi^* \psi$ and the presence of either of these signs makes no difference. If one defines a set of parabolic co-ordinates at each center as

$$\mu_A = r_A(1 + \cos \theta_A), \lambda_A = r_A(1 - \cos \theta_A), \varphi$$

and the same for the B center, Then again by taking limits one finds

$$\lim_{r_{AB} \rightarrow \infty} \xi = 1 + \frac{\lambda_A}{r_{AB}} \quad \text{or} \quad 1 + \frac{\lambda_B}{r_{AB}}$$

$$\lim_{r_{AB} \rightarrow \infty} \eta = - \left(1 - \frac{\mu_A}{r_{AB}} \right) \quad \text{or} \quad 1 - \frac{\mu_B}{r_{AB}}$$

$$\lim_{r_{AB} \rightarrow \infty} \varphi = \varphi$$

Changes in the various quantum numbers during this process may again be found by an examination of the nodes. The n_p remain unchanged, all the n_ξ get converted into n_λ but since the n_η are a family of hyperboloids of revolution, it would be expected therefore, when separation is effected, that if n_η happens to be even, one half of these would go with one nucleus, and the other half with the other nucleus, i.e. $n_\eta \rightarrow 2n_\mu$; however, if n_η is odd then one of the hyperboloids, stays in the middle, and a node appears there; either side of which the wave function takes on positive and negative signs, thus corresponding to the anti-symmetric state. One has now a system of a proton and an hydrogen atom, with total number of nodes equal to $(n_\lambda + n_p + 2n_\mu + 1)$ or $(n_\lambda + n_p + 2n_\mu + 2)$. The energy being that of the hydrogen atom, the expression for which is well known, and so are the corresponding eigenfunctions.

$$E = \frac{R}{(n_\lambda + n_p + 2n_\mu + 1)^2} \quad \text{or} \quad \frac{R}{(n_\lambda + n_p + 2n_\mu + 2)^2}$$

One therefore has a knowledge of the system, at the two extreme ends, and the corresponding wave functions exactly.

The next step is to move a bit from either extremes, immediately potential energy terms of the type $V = -\frac{e}{r_A} - \frac{e}{r_B}$ begin to appear in the Hamiltonian, and one then uses the extreme wave functions for a degenerate perturbation calculation, and thus obtains a few more points close to the ends (one cannot carry out these calculations too far in because the perturbation terms become very large). Then with the extreme ends, and the few other points calculated, one can draw a smooth curve, which can be used to calculate the energy at any internuclear distance.

Using this method Morse and Stueckelberg found a very close similarity with the $1s\sigma$ state obtained by Burrau. They also found that minima appear only in the $1s\sigma$, $3d\sigma$ and $4f\sigma$ states. Therefore to this degree of approximation, the molecule H_2^+ is only stable in these states.

Gullimin and Zeners Variational Study:-

About the same time as Morse and Stueckelberg carried out the above analysis, Gullimin and Zener⁽⁷⁾, carried out a variational study of the molecule, and used the same line of arguments to arrive at an initial guess function. These arguments are as follows:

(1) The differential equation describing the hydrogen molecular ion, is separable into elliptic co-ordinates ξ and η , suggesting thereby the possibility of taking for the eigenfunction a product of two co-ordinate functions.

$$\psi = \sum (\xi) H(\eta)$$

The absence of degeneracy in the ground state function strengthens the assumption, as it precludes the necessity of having to take linear combination of all degenerate states, and thereby making the above factorization impossible

- (2) The η equation being even in η , undergoes no transformation when operated upon by the inversion operator or $\psi(\eta) = \psi(-\eta)$ enabling one to take either the positive or the negative function with equally good assurance of describing the species, but the complete absence of nodes in the ground state, favors a positive function.
- (3) Reduction of the internuclear distance to zero results in the production of a He^+ ion, having a hydrogenic wave function, with a nuclear charge of 2

$$\frac{1}{\sqrt{\pi}} e^{-2r}$$

where r is the distance of the electron from the middle of the nuclear axis. For an infinite separation however, one gets a hydrogen atom at A and a proton at B or vice versa, which obliges one to take a linear combination of the type

$$\frac{1}{4\sqrt{\pi}} (e^{-r_A} + e^{-r_B})$$

Conversion to elliptical co-ordinates defined earlier, gives

$$\psi = C(\alpha\beta\gamma) e^{-1/2 \pi_{AB} \alpha \xi} (e^{-1/2 \pi_{AB} \beta \eta} + e^{1/2 \pi_{AB} \beta \eta})$$

Here one can say that

$$\alpha \Big|_{\pi_{AB}=0} = 0 \quad \alpha \Big|_{\pi_{AB}=\infty} = 1 \quad \beta \Big|_{\pi_{AB}=\infty} = 1$$

Taking limits of this function, one finds

$$\lim_{\pi_{AB} \rightarrow 0} \frac{1}{2} \pi_{AB} \alpha \xi = 2x$$

$$\lim_{\pi_{AB} \rightarrow 0} \pi_{AB} \beta \eta = 0$$

$$\lim_{\pi_{AB} \rightarrow \infty} \beta \eta = \pi_A + \pi_B \quad \text{at one center}$$

$$\lim_{\pi_{AB} \rightarrow \infty} \beta \eta = \pi_A - \pi_B \quad \text{at second center}$$

$$\therefore \psi = C(e^{-\pi_A} + e^{-\pi_B}) \quad \text{for } \pi_{AB} = \infty$$

Hence the wave function degenerates into one describing a He^+ ion and one describing a hydrogen atom and a proton, for zero and infinite nuclear separations respectively, therefore satisfying the physical conditions required. This guessed function is then substituted into the expression $\langle \psi | H | \psi \rangle$ and the energy minimized with respect to the α and β parameters (results are tabulated later)

More recent perturbation calculations:-

Although no new numerical

information regarding the hydrogen molecular ion can be obtained

by treating the wave equation by perturbation methods, nevertheless important information regarding the physical form of the ion, was obtained by using such methods, and they also lead to better variational guess functions. The perturbation methods can be applied to many systems for which the wave equation cannot be solved directly, and study of these methods using the hydrogen molecular ion as a test species was considered important from a comparative point of view. Treatment along these lines was first carried out by Pauling (1)(2)

One proceeds then by making reasonable guesses at the wave function for H_2^+ , calculating the dependence of the energy on the internuclear separation r_{AB} , in each case. If the energy passes through a minimum at some value of r_{AB} , the formation of a stable molecule is indicated.

Assuming as a first attempt that the wave function is simply that of an electron localized in a $1s$ -orbital about one of the nuclei say A, one has

$$\psi = u_{1sA} = \pi^{-1/2} e^{-r_A}$$

The energy corresponding to this function is

$$E = \frac{\langle u_{1sA} | H | u_{1sA} \rangle}{\langle u_{1sA} | u_{1sA} \rangle}$$

since u_{1SA} is normalized, the denominator can be set to unity

$$E = \langle u_{1SA} | -\frac{\hbar^2}{8\pi^2 m} \nabla^2 - \frac{1}{r_A} | u_{1SA} \rangle + \langle u_{1SA} | \frac{1}{r_{AB}} | u_{1SA} \rangle - \langle u_{1SA} | \frac{1}{r_B} | u_{1SA} \rangle$$

The first integral here is the energy of the hydrogen atom

$R = -1/2$ atomic units, the second integral is $1/r_{AB}$ by the

application of the Born-Oppenheimer approximation, while the

third integral can be evaluated by using an electrostatic model

ie of having a unit charge at a distance r_{AB} from the center of an electron cloud whose charge density is $\langle u_{1S} | u_{1S} \rangle$

Summing all these integrals together one obtains

$$E = -\frac{1}{2} + \left(1 + \frac{1}{r_{AB}}\right) e^{-2r_{AB}}$$

It is evident that a reduction of r_{AB} to zero would result in an infinite energy value, which in physical terms could be considered as being caused by the penetration of a proton into a negatively charged atmosphere, carrying another proton in its middle, and thereby displaying a complete lack of stability of the H_2^+ molecule. This wave function then does not describe the situation accurately at all.

Two of the essential features would be (1) the possibility that the electron can pass back and forth from one nucleus to the

other and (2) the possibility that the electron will tend to spend much of its time in the region between the two nuclei, where its potential is low. Hence, forming a linear combination of ψ_{1sA} and ψ_{1sB} one obtains the secular equation

$$\begin{pmatrix} H_{AA} - E & H_{AB} - E \\ H_{BA} - \Delta & H_{BB} - E \end{pmatrix} = 0$$

where

$$H_{AA} = \langle \psi_{1sA} | H | \psi_{1sA} \rangle$$

$$H_{AB} = \langle \psi_{1sA} | H | \psi_{1sB} \rangle$$

$$\Delta = \langle \psi_{1sA} | \psi_{1sB} \rangle$$

Δ represents lack of orthogonality of ψ_{1sA} and ψ_{1sB} . Since the two nuclei are identical one has $H_{AA} = H_{BB}$ and since H is hermitian and real $H_{AB} = H_{BA}$, one can obtain two solutions of the secular determinant

$$E_S = \frac{H_{AA} + H_{AB}}{1 + \Delta}$$

$$E_A = \frac{H_{AA} - H_{AB}}{1 - \Delta}$$

These correspond to the wave functions

$$\psi_S = \frac{1}{\sqrt{2 + 2\Delta}} (\psi_{1sA} + \psi_{1sB})$$

$$\psi_A = \frac{1}{\sqrt{2 - 2\Delta}} (\psi_{1sA} - \psi_{1sB})$$

where S and A represent the words symmetric and antisymmetric wave functions respectively. The wave function ψ_s is symmetric in the positional co-ordinates of the two nuclei A and B. This function places the electron with equal probability in the vicinity of each of the two nuclei. Thus in the plane midway between the two protons one has

$$u_{1sA} = u_{1sB} \quad , \text{ and if the two nuclei are far apart, } |\psi_s|^2 \approx 2(u_{1sA})^2 .$$

The electron density in the midplane of the molecule therefore has approximately double the value that would be produced in the same region by a simple 1s orbital. If one carries out the integrations involved in the expression for ψ_s , one obtains

$$E_s = -\frac{1}{2} + \frac{1}{r_{AB}} + \frac{(r_{AB} + 1)e^{-2r_{AB}} - r_{AB}(r_{AB} + 1)e^{-r_{AB}}}{r_{AB}[(1 + r_{AB} + \frac{1}{3}r_{AB}^2)e^{-r_{AB}} + 1]}$$

If r_{AB} is very large, it gives an energy of $-1/2$ which is the energy of an isolated hydrogen atom. As r_{AB} is decreased, the energy passes through a minimum. The calculated equilibrium internuclear distance, and the dissociation energy are comparable in order of magnitude with the experimentally observed values.

By allowing the electron to move in the vicinity of both nuclei one has in effect introduced the resonance integral H_{AB} , which contributes to the formation of a stable bond.

The chief stabilizing factor in this wave function is a reduction of the potential energy when the electron is in between the two nuclei.

The wave function ψ_A is antisymmetric with respect

to interchange of nuclei, and substitution of the integrals H_{AA} and

H_{BA} into the corresponding energy expression, produces an equation

that has the same energy as ψ_S at large internuclear separations, but

is unstable at all smaller separations. The exact calculations

show that the first excited state of H_2^+ resembles this situation

rather closely, and the plot of energy vs internuclear distance has

no minimum.

The physical reason for this instability is obvious

too, because in the middle of the internuclear axis $\psi_A = \psi_B$

hence $\psi_{SA} = \psi_{SB}$ and $\psi_A = 0$, or in other words at this point

the electron cloud vanishes, where it should be the highest, because

the potential energy is lowest. This tends to create a node and

render the system unstable.

In 1927 Unsold (8) carried out a second order

perturbation treatment on the H_2^+ molecule, using the wave function

centered on just one center, and thereby effecting a neglect of the

resonance integral. He found complete agreement between his

energy value and that calculated by Burrau, but this agreement

without consideration of the resonance integral is misleading.

One dimensional treatment of the H_2^+ molecule:-

In the treatment

carried out by Pauling as outlined above, it was observed, that the

binding energy was quite a bit lower than would be expected from experimental studies. Recently however Walsh and Matsen⁽⁹⁾ have suggested, that owing to the presence of strong charges at the points A and B, there will be a strong force tending to make the electron prefer the direction of the internuclear axis, and they describe the low binding energy obtained above to the fact that the wave function lacks a polarization in this direction, and hence they considered hundred percent polarization, by assuming the internuclear axes to lie in X-direction, and carrying out Pauling's treatment in this set up, using one dimensional wave functions. One can calculate the exchange integral; but not the Coulomb integral. Using the exchange integral so obtained and the three dimensional Coulomb integral, these workers report a 37% higher binding energy than the exact value.

Variational Studies of the H_2^+ Molecule:-

The type of wave function that has been used in the Pauling treatment, does not give one accurate description of the species. This discrepancy is not surprising in view of the crudeness of the function. The electronic cloud as given by the wave function, is of the same shape as that obtained by the accurate solution, but it is too small in the region between the two protons, and too large elsewhere.

The simplest improvement is the introduction of a

scale factor \tilde{z} into the hydrogenic $1S$ functions

$$\psi = \frac{1}{\sqrt{N}} (e^{-\tilde{z}r_A} + e^{-\tilde{z}r_B})$$

this gives a parameter \tilde{z} , with respect to which minimization can be effected. This wave function was used by Finkelstein and Horowitz (10), with very marked improvements, as will be seen from the table of comparison to follow (end of Chapter IV).

The value of \tilde{z} that corresponds to the stable H_2^+ molecule is 1.228, in the Pauling function \tilde{z} is given the value unity. The role of this \tilde{z} factor is to bind the electron cloud up more strongly, in the region between the nuclei. At other internuclear distances the optimum value of \tilde{z} has different values. If the internuclear distance is zero, one has an helium ion in its ground state, for which the correct wave function is a $1S$ orbital with a nuclear charge of 2, ie $\tilde{z} = 2$. On the other hand, if the two nuclei are infinitely far apart the wave function must reduce to that of a normal hydrogen atom with $\tilde{z} = 1$. The scale factor \tilde{z} may be regarded as an effective nuclear charge whose value increases, as internuclear distance is decreased, because of the electrical attractions that the nuclei exert on the electron.

Further improvement of the function was effected by replacing the pure $1S$ atomic orbitals, by hybridized atomic orbitals of the type $(1S + C^2p_z)$ where C is a variable parameter

(to be determined by minimizing the energy) and $2p_z$ is a hydrogen like $2p$ atomic orbital, with axis lying along the molecular axis.

The use of this function lies in the fact that the $2p_z$ orbital has a positive lobe, which can be used to increase the electron density in the internuclear region, where the electron wants to be; at the same time the presence of a node at the ends of the bond reduces the probability of finding the electron there; this happens to be the place where the electron wants to be least. The $2p_z$ function can be said to make possible the mutual polarization of the two atomic orbitals.

Dickinson ⁽¹¹⁾ has calculated the energy corresponding to the hybridized function.

$$\psi = \frac{1}{\sqrt{N}} \left(e^{-z r_A} + C r_A \cos \theta_A e^{-\xi z r_A} + e^{-z r_B} + C r_B \cos \theta_B e^{-z r_B} \right)$$

This function involves three parameters ξ , C , and ξ , where θ_A and θ_B are the angles between the internuclear axis, and the lines joining the nuclei to the electron. This wave function does indeed as expected move the electron into the middle and away from the two ends.

Hurley ⁽¹²⁾ used a slightly different technique to increase the electronic cloud in the middle; He used the same kind of wave function as used by Pauling, except he centered them at a distance λ , inside from each nucleus.

$$\psi = \frac{1}{\sqrt{N}} \left(e^{-z r_A'} + e^{-z r_B'} \right)$$

where r_a' and r_b' are the distances of the electron as measured from the displaced centers. Using this wave function Hurley carried out a minimization with respect to χ and Z , and found the electronic cloud almost identical with the exact theoretical calculation. Unfortunately this wave function is not very accurate close to the nuclei, at the same time some of the integrals are very difficult to evaluate owing to the presence of the factor χ .

(13)

James has used a very simple function of the type

$$\psi = \frac{1}{\sqrt{N}} \exp[-Z(r_a + r_b)]$$

The quantity $r_a + r_b$ has its minimum value along the straight line segment drawn between the two nuclei, and it is constant at all points along this line. Therefore the above function is constant, and has its maximum value along the axis of the bond; obviously it overdoes the concentration of electrons in the bond. Furthermore it does not lead to the correct wave function in the limit of large internuclear distance. James found that this simple function is as good as the Finkelstein - Horowitz LCAO function if the nuclei are not too far apart.

The United Atom Treatment:-

Since the LCAO approximation when applied to H_2^+ molecule is simpler than the calculations of Burrau and of Charkravarty but the results are not as accurate, Matsen carried out a simple treatment (called the united atom treatment) which gives results in good agreement with the accurate calculations. This method consists in representing the

(19)

states of H_2^+ by atomic orbitals centered at the middle of the bond.

Matsen did a perturbation calculation with such atomic orbitals. The Hamiltonian is written as

$$-\frac{\nabla^2}{2} - \frac{Z}{r} \left(+ \frac{Z}{r_A} - \frac{1}{r_A} - \frac{1}{r_B} \right)$$

where r is the distance between the electron and the midpoint between nuclei A and B. The first two terms in the Hamiltonian make up H and the last three H' . The zero order functions are the hydrogen like wave functions with charge Z . For these states to which first order non-degenerate perturbation theory can be applied, the energy is found with the help of the virial theorem

$$E_{n\ell m} = \frac{Z^2}{2n^2} - 2 \left\langle \psi_{n\ell m} \left| \frac{1}{r_A} \right| \psi_{n\ell m} \right\rangle$$

where $Z = 2$, this produces very good results at short internuclear distances. Matsen found that by carrying out a variational treatment with respect to the Z parameter, one could improve the energy.

The Use of Gaussian Functions

On examination of the wave functions that have been used in all the treatments given above, one finds that essentially all of these are of the form $N e^{-C/r}$ or linear combinations thereof, these generally result (15) in integrals which are very difficult to evaluate. Boys for the first time demonstrated a method of successive approximation by which the stationary state electronic wave function for any configuration of atoms can be calculated to any desired degree of accuracy by inclusion of a sufficient number of terms. This method does not depend on any numerical integration.

Boys for the first time showed that all integrals between Gaussian

functions and Schrödinger operators can be evaluated very readily, the most complicated being that of the electronic interactions between one product of two Gaussians on different centers, with another product of two other Gaussians. These integrals and the simpler ones required were all evaluated explicitly in this paper.

Boys proposed that these Gaussian functions in the most general case be compounded into Slater determinants, followed by evaluation of integrals and minimization of the energy by the Ritz variational method, which consists in evaluating the integrals with a trial function (in this case the Gaussians) that depend on a number of parameters, and varying these parameters until the expectation value of the energy is a minimum. The result is an upper limit to the ground state energy of the system, which is likely to be close if the form of the trial function resembles that of the eigenfunction⁽¹⁶⁾.

Several approximate and non-converging methods of evaluating wave functions of molecules have been widely used for making deductions on the general nature of molecules. The best known of these are the molecular orbital and the localized bond methods. It has, however, never been possible to make a prior predictions by such procedures in cases other than the very simplest, since the requisite integrals could not be evaluated, and had

to be estimated empirically. However, if the orbitals used in any of these cases were taken to be linear combinations of functions derived from Gaussian functions all the required integrals could be evaluated explicitly. The analysis given by Boys therefore provides for the first time a method of applying quantitatively, and in a fundamental way, the approximate methods of the molecular orbital and localized bond types.

Prior to the announcement of Boys, the only cases where explicit methods were available without numerical integration, were for the two electron problem as He and H_2 but no converging methods were available for more general molecules.

One can define the complete class of Gaussian functions to consist of all functions, and of all linear combinations of functions of the type $\chi^l y^m z^n \exp(-a r_A^2)$ where l, m, n , have any integral values, and "a" has any positive value, and one has the general notation.

$$\chi_A = \chi - A_x \text{ etc} \qquad r_A^2 = x_A^2 + y_A^2 + z_A^2$$

and where A_x, A_y, A_z have any real values. By taking these functions and multiplying them by α and β i.e. spin up or spin down functions one can very readily construct the Slater determinants, and the Schrodinger integrals between them can be readily evaluated, the only step of difficulty being the evaluation of the integral of

the type

$$\langle g_r | g_s \rangle \quad \langle g_r | K | g_s \rangle \quad \langle g_r | V | g_s \rangle \quad \langle g_r g_s | M | g_t g_u \rangle$$

where g_r , g_s , g_t and g_u are members of the complete class of Gaussian functions. K , V , and M correspond to kinetic and potential energy operators respectively. If the integrals belonging to this class of Gaussians are evaluated using simple functions of the type e^{-ax^2} then one can easily derive the integrals for the general class by differentiation with respect to the parameters in the integral formulae, followed by taking appropriate linear combinations.

One might then say that the introduction of these Gaussian functions, has for the first time provided one with a quantitative method of studying any nuclear frame work, and there is no need to resort to very complicated numerical integrations, as one had to in the case of the more conventional wave functions that were used in the past.

Following Boys announcement of the Gaussian integrals these wave functions were used very effectively by Meckler⁽¹⁷⁾ for calculating the oxygen electronic levels.

In a later communication Boys⁽¹⁸⁾ showed that the Gaussians can be suitably modified to include correlation

terms of the type $g_{ij} x_{ij}^2$ (x_{ij} = distance between the i^{th} and j^{th}

electrons) and still the integrals reduce to a product of elementary functions and error functions.

Finally Singer⁽¹⁹⁾ has shown by a different method that the potential energy integrals associated with the most general kind of Gaussian functions.

$$\psi = \sum_R C_R \phi_R = \sum_R P_R \exp(-Q_R)$$

can be reduced to simple numerical quadratures (Q_R is any positive definite quadratic form in the space co-ordinates of n electrons, P_R is a polynomial in $3m$ ($m \leq n$) co-ordinates).

The absence of any restriction on the nature of Q_R leads to a very interesting feature ie one can study functions of non-spherical nature, since actually in Boys studies only spherical Gaussian could be considered. By using Singers modifications it is possible to consider Gaussian with an ellipsoidal symmetry, and thus introduce into the wave functions a certain degree of polarization.

The present investigation then was carried out on the hydrogen molecular ion to study how spherical, ellipsoideal and hybridized Gaussians could be used, with a view to obtaining their relative merits as variational wave functions

CHAPTER II

GENERAL METHODS

Methods of Integration:-

In the present investigation the following functions, centered on the individual nuclei were used:-

$$(1) \quad e^{-m_k r^2}$$

$$(2) \quad e^{-m_k (x^2+y^2) - \frac{1}{2} m_k z^2}$$

$$(3) \quad r \cos \theta e^{-a_k r^2}$$

The method consisted of determining integrals of the following type:-

$$\langle \psi | \psi \rangle \quad \langle \psi | -\frac{\nabla^2}{2} | \psi \rangle \quad \langle \psi | \frac{1}{r_A} | \psi \rangle \quad \text{and} \quad \langle \psi | \frac{1}{r_B} | \psi \rangle$$

The integrals for the first type of wave function were easily obtained by straight forward integration between appropriate limits, as demonstrated by Boys⁽¹⁵⁾, and resulted in products of constants with each other, with the error function, and the exponential function. The error function was determined by an extension of the method given by Hastings⁽¹⁹⁾, while the exponential function was evaluated by multiplication of appropriate tabulated values.

The integrals for the third type, were obtained quite readily from those of the first kind, by a simple process of

differentiation as follows:-

If one defines the following, in the manner done by Boys⁽¹⁵⁾:-

$$r_A^2 = x_A^2 + y_A^2 + z_A^2 \quad \text{with } x_A^2 = (x - Ax)^2 \text{ etc.}$$

$$r_B^2 = x_B^2 + y_B^2 + z_B^2 \quad \text{with } x_B^2 = (x - Bx)^2 \text{ etc.}$$

then:-

$$\langle z_A e^{-a_K r_A^2} | H | e^{-m_L r_B^2} \rangle = -\frac{1}{2a_K} \frac{\partial}{\partial A_z} \langle e^{-a_K r_A^2} | H | e^{-m_L r_B^2} \rangle$$

$$\langle z_A e^{-a_K r_A^2} | H | z_B e^{-a_L r_B^2} \rangle = -\frac{1}{4a_K} \frac{\partial^2}{\partial A_z \partial B_z} \langle e^{-a_K r_A^2} | H | e^{-a_L r_B^2} \rangle$$

In the case of the second type of wave function, the overlap and the kinetic energy integrals can be obtained by straight forward integration; however the potential energy integrals, have to be evaluated, by a slightly simplified form of the method given by Singer (18).

The main value of Singer's technique lies in the fact that it can be used for the most generalized form of gaussian functions eg. any function of the type

$$\psi = \sum_K C_K \phi_K = \sum_K P_K \exp(-Q_K)$$

where Q_K is any positive definite quadratic form in the space

co-ordinates of n electrons, P_k is a polynomial in $3n$ co-ordinates.

Suppose then one is interested in the evaluation of the potential energy integral

$$\left\langle e^{-Q_A} \left| \frac{1}{r_c} \right| e^{-Q_B} \right\rangle$$

where C is the position of the nucleus, and A and B are the centers of two gaussians respectively, one has then

$$\begin{aligned} \exp(-Q_A) &= \exp(-(ax_A^2 + cy_A^2 + fz_A^2)) \\ \exp(-Q_B) &= \exp(-(bx_B^2 + dy_B^2 + gz_B^2)) \end{aligned}$$

For a single electron problem such as the present one, let the electronic and nuclear co-ordinates be x, y, z , and C_x, C_y, C_z respectively. Then from vectorial considerations one has:-

$$Q_A = (\tilde{x} - \tilde{A}) \underline{\alpha} (\tilde{x} - \tilde{A}) \quad ; \quad Q_B = (\tilde{x} - \tilde{B}) \underline{\beta} (\tilde{x} - \tilde{B})$$

where $\underline{\alpha}$ and $\underline{\beta}$ are the diagonal matrices

$$\underline{\alpha} = \begin{pmatrix} a & 0 & 0 \\ 0 & c & 0 \\ 0 & 0 & f \end{pmatrix} \quad \underline{\beta} = \begin{pmatrix} b & 0 & 0 \\ 0 & d & 0 \\ 0 & 0 & g \end{pmatrix} \quad (\sim \text{refers to transpose})$$

By carrying out the matrix-vector multiplication in (1) one has

$$\begin{aligned} Q_A &= \tilde{x} \underline{\alpha} \tilde{x} - 2 \tilde{x} \underline{\alpha} \tilde{A} + \tilde{A} \underline{\alpha} \tilde{A} \\ \text{Let } \underline{\alpha} \tilde{A} &= \tilde{e}_A \quad \text{and} \quad \tilde{A} \underline{\alpha} \tilde{A} = G_A \\ \therefore Q_A &= \tilde{x} \underline{\alpha} \tilde{x} - 2 \tilde{e}_A \tilde{x} + G_A \\ Q_B &= \tilde{x} \underline{\beta} \tilde{x} - 2 \tilde{e}_B \tilde{x} + G_B \end{aligned}$$

$$\therefore \langle e^{-Q_A} | 1/n_c | e^{-Q_B} \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\tilde{x}(\alpha+\beta)\tilde{x} - 2(\tilde{e}_A + \tilde{e}_B)\tilde{x} - G_A + G_B} d\tilde{x}$$

By defining the following:

$$\underline{\alpha} + \underline{\beta} = \underline{D}$$

$$\tilde{e}_A + \tilde{e}_B = \tilde{e}$$

$$Q = Q_A + Q_B = \tilde{x} \underline{D} \tilde{x} - 2 \tilde{e} \tilde{x} + G$$

$$\tilde{p} = \underline{D}^{-1} \tilde{e}$$

and

$$G' = G - \tilde{e} \underline{D}^{-1} \tilde{e}$$

One has

$$\underline{D}^{-1} = (\underline{\alpha} + \underline{\beta})^{-1}$$

$$\therefore \tilde{e} \underline{D}^{-1} \tilde{e} = \frac{(aA_x + bB_x)^2}{(a+b)} + \frac{(cA_y + dB_y)^2}{(c+d)} + \frac{(fA_z + gB_z)^2}{(f+g)}$$

But from the definition of \tilde{p} one has

$$\begin{aligned} \tilde{e} &= \underline{D} \tilde{p} \\ \tilde{e} &= \tilde{p} \underline{D} = \tilde{p} \underline{D} \end{aligned} \quad (\text{since } \underline{D} \text{ is diagonal})$$

$$\therefore G' = G - \tilde{p} \underline{D} \tilde{p} = G - \tilde{p} \underline{D} \tilde{p}$$

$$\text{or } G = G' + \tilde{p} \underline{D} \tilde{p}$$

$$\begin{aligned}\therefore Q &= \tilde{x} \underline{D} \tilde{x} - 2\tilde{p} \underline{D} \tilde{x} + \tilde{p} \underline{D} \tilde{p} + G' \\ &= (\tilde{x} - \tilde{p}) \underline{D} (\tilde{x} - \tilde{p}) + G'\end{aligned}$$

If the vector between the origin of the co-ordinates and the electron be represented by \vec{r} and that between the origin and the nucleus by \vec{c} , then the vector between the electron and the nucleus will be

$$\begin{aligned}\vec{r}_e &= \vec{r} - \vec{c} \\ \therefore r_e &= |\vec{r} - \vec{c}| \end{aligned}$$

using the identity

$$\frac{1}{f} = \pi^{-1/2} \int_{-\infty}^{\infty} \exp(-u^2 f^2) du$$

one has

$$\frac{1}{|\vec{r} - \vec{c}|} = \pi^{-1/2} \int_{-\infty}^{\infty} \exp[-u^2 |\vec{r} - \vec{c}|^2] du$$

$$\therefore |\vec{r} - \vec{c}|^2 = (x - c_x)^2 + (y - c_y)^2 + (z - c_z)^2$$

Defining:

$$\vec{b} = \vec{c} - \vec{p}$$

One has

$$\begin{aligned}c_x &= b_x + p_x \\ c_y &= b_y + p_y \\ c_z &= b_z + p_z\end{aligned}$$

$$\begin{aligned}\frac{1}{|\vec{r} - \vec{c}|} &= \frac{1}{r_e} \\ &= \pi^{-1/2} \int_{-\infty}^{\infty} \exp \left\{ -u^2 \left[(x - p_x)^2 + b_x^2 - 2b_x(x - p_x) + (y - p_y)^2 + b_y^2 \right. \right. \\ &\quad \left. \left. - 2b_y(y - p_y) + (z - p_z)^2 + b_z^2 - 2b_z(z - p_z) \right] \right\} du\end{aligned}$$

Substitution of this into the operator part of the integral under investigation yields,

$$\langle e^{-QA} | 1/\pi | e^{-QB} \rangle = \pi e^{-G'} \int_{-\infty}^{\infty} \frac{\exp \left[-\frac{u^2 b_x^2 (a+b)}{a+b+u^2} - \frac{u^2 b_y^2 (c+d)}{c+d+u^2} - \frac{u^2 b_z^2 (f+g)}{f+g+u^2} \right]}{[(a+b+u^2)(c+d+u^2)(f+g+u^2)]^{1/2}} du$$

Changing variables, by making the substitution

$$u = (f+g)^{1/2} y (1-y)^2$$

one gets,

$$2\pi \exp \left\{ \frac{-ab(A_x-B_x)^2}{a+b} - \frac{cd(A_y-B_y)^2}{c+d} + \frac{fg(A_z-B_z)^2}{f+g} \right\} \times \int_0^1 \frac{\exp \left\{ -\left[\frac{(a+b)b_x^2}{(a+b)+\{(f+g)-(a+b)\}y^2} + \frac{(c+d)b_y^2}{(c+d)+\{(f+g)-(c+d)\}y^2} \right] \right\} (f+g)y^2 dy}{[(a+b)+\{(f+g)-(a+b)\}y^2]^{1/2} [(c+d)+\{(f+g)-(c+d)\}y^2]^{1/2}}$$

Under the conditions dictated by the second form of function. used in this work, one has $(a+b) = (c+d) \neq (f+g)$ which can be achieved by setting $a=c$ and $b=d$

$$\therefore \langle e^{-a(x_A^2+y_A^2)-fz_A^2} | 1/\pi | e^{-b(x_B^2+y_B^2)-gz_B^2} \rangle = 2\pi \exp \left\{ \frac{-ab}{a+b} [(A_x-B_x)^2 + (A_y-B_y)^2] - \frac{fg(A_z-B_z)^2}{f+g} \right\} \int_0^1 \frac{\exp \left\{ -\left[\frac{(a+b)(b_x^2+b_y^2)}{(a+b)(f+g)-(a+b)y^2} + b_z^2 \right] (f+g)y^2 \right\}}{[(a+b)+\{(f+g)-(a+b)\}y^2]^{1/2}} dy$$

The last integral in this expression cannot be analytically evaluated and one is obliged to carry out a numerical integration.

During the course of the present investigation the Gaussian quadrature method as described by Hartree ⁽²¹⁾ was used.

This method consists essentially of using a finite number of values of the integrand, and may be regarded as giving a weighted mean of these values.

$$\int_a^b f(x) dx = (b-a) \left[\sum_k w_k f(x_k) \right] \quad (2)$$

where the w_k s are the weights assigned to the values of the integrand at points x_k .

Introduction of the new variable

$$\xi = [2x - (a+b)] / (b-a) \quad (3)$$

transforms the limits of integration to -1, +1, and the integral becomes:

$$\int_a^b f(x) dx = \frac{b-a}{2} \int_{-1}^{+1} f\left\{\frac{2\xi - (a+b)}{b-a}\right\} d\xi = \int_{-1}^{+1} \phi(\xi) d\xi \quad (4)$$

The method next consists of replacing the function $\phi(\xi)$ by a function that can be expanded into a series of the type (2)

$$\int_{-1}^{+1} \phi(\xi) d\xi = 2 \sum_k w_k \phi(\xi_k) \quad (5)$$

Suppose that the value of ξ is known at $(n+1)$ points, then it will be

shown that one can replace $\phi(\xi)$ by a polynomial $P_{2n+1}(\xi)$ where $2n+1$ is the order of this polynomial. Let $P_n(\xi)$ be a Legendre polynomial of order n ; then from a well known orthogonality relation one has

$$\int_{-1}^{+1} P_n(\xi) P_m(\xi) d\xi = \delta_{mn} \quad (6)$$

Dividing $P_{2n+1}(\xi)$ by $P_n(\xi)$ gives

$$\frac{P_{2n+1}}{P_{n+1}(\xi)} = q_n(\xi) + \frac{r_n(\xi)}{P_{n+1}(\xi)} \quad (7)$$

where $q_n(\xi)$ and $r_n(\xi)$ are the quotient and remainder polynomials respectively, of orders n , which can be proved by induction.

$$\therefore P_{2n+1}(\xi) = P_{n+1}(\xi) q_n(\xi) + r_n(\xi) \quad (8)$$

Since the Legendre functions form a complete set, the function

$q_n(\xi)$ can be represented as a linear combination of these

$$q_n(\xi) = \sum_{m=1}^n c_m P_m(\xi) \quad (9)$$

since m is never allowed to equal $(n+1)$ it is obvious that the integral

$$\int_{-1}^{+1} P_{n+1}(\xi) q_n(\xi) d\xi = 0 \quad (10)$$

Hence integration of both sides of (8) gives

$$\int_{-1}^{+1} p_{2n+1}(\xi) d\xi = \int_{-1}^{+1} x_n(\xi) d\xi \quad (11)$$

If one therefore intends to use the polynomial $P_{2n+1}(\xi)$ in place of the function $\phi(\xi)$ one will get from equation (2)

$$\int_{-1}^{+1} p_{2n+1}(\xi) d\xi = 2 \sum_k W_k [P_{n+1}(\xi_k) q_n(\xi_k) + x_n(\xi_k)] \quad (12)$$

But equation (10) had proved the integral to be independent of the polynomial $q_n(\xi)$, hence one is obliged to take the values of ξ_R which are the roots of the Legendre polynomial $P_{n+1}(\xi)$ because at these points this function vanishes.

Suppose one defines another polynomial

$$F_{n+1}(\xi) = (\xi - \xi_1)(\xi - \xi_2) \dots (\xi - \xi_{n+1}) \quad (13)$$

then an expansion of the fraction $x_n(\xi)/F_{n+1}(\xi)$ into partial fractions yields

$$x_n(\xi) = \sum_k \frac{F_{n+1}(\xi)}{F'_{n+1}(\xi_k)(\xi - \xi_k)} x_n(\xi_k) \quad (14)$$

$$\int_{-1}^{+1} x_n(\xi) d\xi = \sum_k \int_{-1}^{+1} \frac{F_{n+1}(\xi)}{F'_{n+1}(\xi_k)(\xi - \xi_k)} d\xi \quad (15)$$

Then from formulae (11) and (12)

The weights W_k are given by

$$\int_{-1}^{+1} g_n(\xi) d\xi = 2 \sum_R W_R g_n(\xi_R)$$

and comparison with (15) gives the values

$$W_k = \frac{1}{2} \int_{-1}^{+1} \frac{F_{n+1}(\xi) d\xi}{F'_{n+1}(\xi_k)(\xi - \xi_k)}$$

The values of W_k and ξ_k for Gaussian quadrature formulae up to $n = 16$ (17)

have been tabulated by Lowan, Davids and Levenson and were the ones used during the present investigation.

The method of energy minimization was carried out in two parts:

(1) Minimization of the linear parameters:-

This is essentially a solution of the matrix equation of the type:-

$$(\underline{H} - E\underline{S}) \vec{C} = 0 \quad (17)$$

Where \underline{H} is the matrix representation of the Hamiltonian operator under the chosen set of basis functions, \underline{S} is a matrix representation of 1, the identity operator, under the same set, \vec{C} is a vector, the components of which are the linear parameters to be optimized, and E is the eigenvalue corresponding to a given \vec{C} vector. The minimization procedure then essentially consists in the generation of a \vec{C} vector which will give the lowest E value which might be said to correspond to the ground state energy.

An examination of equation (17) shows, that it can hold either if the vector C or the determinant is zero

$$|\underline{H} - E\underline{S}| = 0 \quad (18)$$

the former of course corresponds to an uninteresting trivial case and hence, one has to look for vanishing determinant. It is obvious then that (18) is a polynomial having several roots corresponding to each there being a separate \vec{C} vector, and hence to generalize even further one may replace the \vec{C} vector by a matrix \underline{C} compounded from several vectors, \vec{C} each corresponding to a given value of E

$$(\underline{H} - \underline{E}\underline{S}) \underline{C} = 0 \quad (19)$$

where E also takes on matrix form, being diagonalized with the diagonal elements, equal to the eigenvalues.

The method used for the solution of the matrix equation was the Jacobi method; but unfortunately this cannot handle a problem where the \underline{S} matrix is not a unit matrix. Let us then examine a slightly different problem.

$$\underline{\tilde{m}} \underline{H} \underline{m} \underline{\lambda} = \underline{E} (\underline{\tilde{m}} \underline{S} \underline{m}) \underline{\lambda} \quad (20)$$

Where \underline{m} and $\underline{\lambda}$ are new matrices, the commutation of \underline{E} and \underline{m} being permissible since the former is a diagonal matrix. The matrix \underline{m} is so chosen that $\underline{\tilde{m}} \underline{S} \underline{m} = \underline{1}$

This process of reduction to a unit matrix is known

as the Schmidt orthogonalization process. It is a stepwise conversion of a set of non-orthonormalized functions into an orthonormal basis set. Suppose one has two non-orthonormal functions χ_1 , and χ_2 such that

$$\langle \chi_1 | \chi_1 \rangle \neq 1$$

$$\langle \chi_1 | \chi_2 \rangle \neq 0$$

$$\langle \chi_2 | \chi_2 \rangle \neq 1$$

then one can form by taking appropriate linear combination of these; two other functions χ'_1 and χ'_2 in the manner

$$\chi'_1 = a\chi_1 \tag{22}$$

$$\chi'_2 = c\chi_1 + d\chi_2 \tag{23}$$

such that

$$\langle \chi'_1 | \chi'_1 \rangle = 1 \tag{24}$$

$$\langle \chi'_1 | \chi'_2 \rangle = 0 \tag{25}$$

$$\langle \chi'_2 | \chi'_2 \rangle = 1 \tag{26}$$

This then gives one three unknown linear parameters, a , c , and d and three simultaneous equations (24), (25) and (26) from which they can be readily evaluated. If one writes the original S matrix from the non-orthonormalized set in the form

$$\underline{S} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} = \begin{pmatrix} \langle x_1 | x_1 \rangle & \langle x_1 | x_2 \rangle \\ \langle x_2 | x_1 \rangle & \langle x_2 | x_2 \rangle \end{pmatrix}$$

one has essentially by a Schmidt orthogonalization, converted into

$$\begin{pmatrix} \langle ax_1 | ax_1 \rangle & \langle ax_1 | cx_1 + dx_2 \rangle \\ \langle cx_1 + dx_2 | ax_1 \rangle & \langle cx_1 + dx_2 | cx_1 + dx_2 \rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

The origin of this matrix becomes clear, by referring to Dirac's ⁽²⁰⁾ dual vector space system of bras and kets in the following matrix equation

$$\begin{pmatrix} a & 0 \\ c & d \end{pmatrix} \begin{pmatrix} \langle x_1 | x_1 \rangle & \langle x_1 | x_2 \rangle \\ \langle x_2 | x_1 \rangle & \langle x_2 | x_2 \rangle \end{pmatrix} \begin{pmatrix} a & c \\ 0 & d \end{pmatrix} = \begin{pmatrix} \langle ax_1 | ax_1 \rangle & \langle ax_1 | cx_1 + dx_2 \rangle \\ \langle cx_1 + dx_2 | ax_1 \rangle & \langle cx_1 + dx_2 | cx_1 + dx_2 \rangle \end{pmatrix}$$

Where the matrix on the left has been multiplied into the bra part, while the one on the right into the ket part of the dot product. These two left and right matrices are the m matrices of equation (21).

Now multiplying both sides of (21) by $\tilde{\lambda}$ on the left

$$\tilde{\lambda} \underline{m} \underline{H} \underline{m} \underline{\lambda} = \tilde{\lambda} \underline{E} \underline{\lambda} = \underline{E} \tilde{\lambda} \underline{\lambda}$$

since $\underline{\lambda}$ is unitary and

$$\sum \lambda = 1.$$

The $\underline{\Lambda}$ matrix is so chosen that the matrix product

$$\underline{\tilde{\lambda}} \underline{\tilde{m}} \underline{H} \underline{m} \underline{\lambda}$$

is diagonalized, then the resulting diagonal elements will be equal element by element to the matrix \underline{E} and hence the eigenvalues E are known, once the matrix $\underline{\tilde{m}} \underline{H} \underline{m}$ has been diagonalized.

From equation (19) one has again

$$\underline{H} \underline{C} = \underline{E} \underline{S} \underline{C}$$

It follows from comparison with the preceding equation that:

$$\underline{C} = \underline{\tilde{m}} \underline{\lambda}$$

Hence the vector corresponding to the lowest diagonal element in \underline{E} will contain the best set of $\underline{\tilde{C}}$ values for a minimization of energy.

(2) Minimization of the exponential parameters:-

The exponential parameters of the wave functions were minimized quite readily by a method of Quadratic Minimization due to Ransil (18), which assumes a parabolic energy surface in hyper space:-

This method consists of effecting a MacLaurin expansion of the energy function very close to the minimum. Considering the energy to be a function of two exponential variables only, m_1 and m_2 one can construct a three dimensional plot, which will represent the energy surface for a given functional form, and a given pair of numbers m_1 and m_2 will determine the minimum of this surface. Expressing the energy as a function of two variables in the form $E(m_1, m_2)$ a MacLaurin expansion about the zero point can be readily obtained:

$$E(m_1, m_2) = E_0 + \sum_i \left(\frac{\partial E}{\partial m_i} \right)_0 \Delta m_i + \frac{1}{2} \sum_i \sum_j \frac{\partial^2 E}{\partial m_i \partial m_j} \Delta m_i \Delta m_j$$

Then applying the minimization criterion of

$$\delta E = 0$$

one gets

$$\delta E = \delta E_0 + \sum_i \left(\frac{\partial E}{\partial m_i} \right)_0 \delta(\Delta m_i) + \frac{1}{2} \sum_i \sum_j \left(\frac{\partial^2 E}{\partial m_i \partial m_j} \right) \left[\delta(\Delta m_i) \Delta m_j + \Delta m_j \delta(\Delta m_i) \right] = 0$$

Since E is a constant and i and j are dummy indices which can be readily interchanged, one can simplify the above equation to

$$\begin{aligned} \delta E &= \sum_i \left(\frac{\partial E}{\partial m_i} \right)_0 \delta(\Delta m_i) + \sum_i \sum_j \left(\frac{\partial^2 E}{\partial m_i \partial m_j} \right) \Delta m_j \delta(\Delta m_i) \\ &= \sum_i \left[\left(\frac{\partial E}{\partial m_i} \right)_0 + \sum_j \left(\frac{\partial^2 E}{\partial m_i \partial m_j} \right) \Delta m_j \right] \delta(\Delta m_i) = 0 \quad (27) \end{aligned}$$

This equation now implies that either all Δm_i are zero and no incrementation of the parameters have been effected or that the coefficients of (27) are vanishing, the former of course corresponds to a trivial case, and the problem reduces to one of the type

$$\frac{\partial E}{\partial m_i} = - \sum_j \frac{\partial^2 E}{\partial m_i \partial m_j} \Delta m_j \quad i=1, 2$$

This can then be written in matrix form:

$$\begin{pmatrix} \frac{\partial E}{\partial m_1} \\ \frac{\partial E}{\partial m_2} \end{pmatrix} = - \begin{pmatrix} \frac{\partial^2 E}{\partial m_1^2} & \frac{\partial^2 E}{\partial m_1 \partial m_2} \\ \frac{\partial^2 E}{\partial m_2 \partial m_1} & \frac{\partial^2 E}{\partial m_2^2} \end{pmatrix} \begin{pmatrix} \Delta m_1 \\ \Delta m_2 \end{pmatrix} \quad (28)$$

The problem is then, one of calculating the "best" set of increments Δm_1 and Δm_2 as shown in the vector, on the right hand side of (28).

For a given set of m and Δm values, which should be very close to the minimum one proceeds to evaluate the elements of the matrix in the above equation (24) with the help of Newton's interpolation formulae for one and two variables; and are of the following forms:-

$$\frac{\partial E}{\partial m_i} = [E(m_1 \dots m_i + \Delta m_i \dots m_n) - E(m_1 \dots m_i - \Delta m_i \dots m_n)] / 2 \Delta m_i$$

$$\frac{\partial^2 E}{\partial m_i^2} = \frac{E(m_1 \dots m_i + \Delta m_i \dots m_n) - 2E(m_1 m_2 \dots m_n) + E(m_1 m_2 - \Delta m_2 \dots m_n)}{\Delta m_i^2}$$

$$\frac{\partial^2 E}{\partial m_i \partial m_j} = \frac{E(m_1 \dots m_i + \Delta m_i \dots m_j + \Delta m_j \dots m_n) - E(m_1 \dots m_i + \Delta m_i \dots m_n) - E(m_1 \dots m_j + \Delta m_j \dots m_n) + E(m_1 m_2 \dots m_n)}{\Delta m_i \Delta m_j}$$

The inverse of the matrix is evaluated and multiplied into the left hand vector, resulting there by in an improved set of parameters, which are added again to the original parameters and an optimized energy calculated.

Programming Procedures:-

For the present project the integrals and the various matrix manipulations involved were programmed for the IBM 1620 made available by the University of Alberta Computing Center. A general flow chart showing the various steps in calculation is shown. Those routines marked with an asteriske, as well as the floating point subroutines used throughout were programmed by F. W. Birss.

Since $(n+1)(n+2)/2$ energy values, were required to effect the Quadratic minimization procedure, the latter was given full control of the program.

The purpose of most of the subroutines is given in the discussion above. The eigenvalue search subroutine, was designed to search for the lowest eigenvalues, and corresponding eigenvectors, and to set these in preassigned positions.

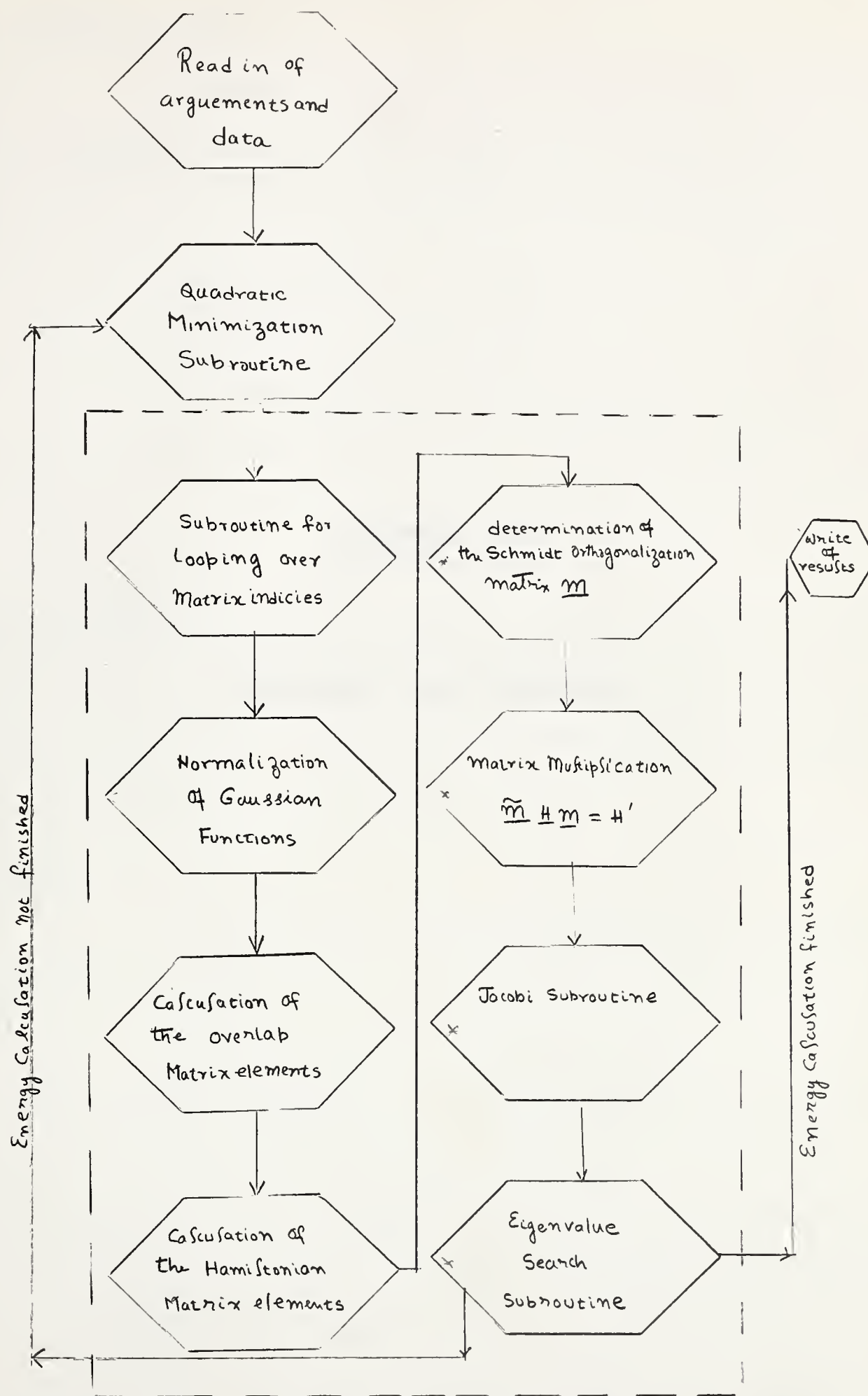


Fig. 1: Generalized Flow Chart for Program used

CHAPTER 111

THE FIRST TRIAL FUNCTION

The Trial Function:-

In order to compare the efficiency of the Gaussian approximation in this simplest molecular problem with the normal approach using Slater type orbitals, a trial function comparable to that of Finkelstein and Horowitz, was chosen. This had the form

$$\psi = \sum_i C_i N_i (e^{-m_i r_A^2} + e^{-m_i r_B^2})$$

The linear parameters (C_i) and the exponential parameters (m_i) were obtained by the method given in Chapter 11. The results obtained are given in Tables I to III. In Table IV are given the results of a calculation of the value of the function along the internuclear axis for the two and three Gaussian combinations at $R=2$. In figure 2 the results for the three Gaussian combinations are plotted with those obtained from the exact and from the Finkelstein - Horowitz treatment; in fig. 3 the results of the two and three Gaussian combinations are plotted for comparison.

Discussion:-

The early study of Pauling⁽¹⁾ on H_2^+ made use of a linear combination of $1s$ orbitals centered on each nucleus. The results however were not very accurate as no allowance had been made for an orbital exponent. The lack of this factor results in a decrease in kinetic energy of the molecule, instead of an increase as might be expected for stable bond formation. The Quantum Mechanical Virial theorem is violated. At an internuclear separation, close to the equilibrium value, the influence of a second nucleus is likely to cause an increase in the amount of positive charge an electron would experience as a result of being in a molecular orbital. The introduction of

an effective nuclear charge at both ends of the molecule would result in an increased attraction for the electron, into the region between the nuclei, and thereby contribute to stable bond formation. Minimization of the energy with respect to these parameters does in fact render the wave function consistent with the virial theorem in keeping with an important theorem, proved for the first time by Fock⁽²²⁾.

As the initial trial value of the exponential parameters in the Gaussian function, the value of the parameters obtained by Longstaff and Singer⁽²³⁾ for the hydrogen atom were scaled to the H_2^+ problem by multiplying by the square of the orbital exponent obtained by Finkelstein and Horowitz who had for the first time realized the necessity for such a parameter. The result for the electronic energy at internuclear distance of two atomic units was found to be -1.0851 a.u., the value of the parameters being $m_1 = 0.7179$ $m_2 = 0.3393$ $m_3 = 0.0358$ for a three Gaussian combination. From an inspection of Table 1 it is obvious that a considerable variation of the exponential parameters was effected to obtain the minimum value of -1.0882 a.u.

The energies obtained for various linear combinations of this type of function, do indeed compare very favorably with the results of Finkelstein and Horowitz. However the value of the function as plotted against distances along the internuclear axis do not compare at all favorably with the exact or the Finkelstein - Horowitz curve.

The character of the values of the wave function along the internuclear axis indicate very clearly that the Gaussian approximation, although leading to a reasonable value for the energy, cannot reproduce in detail the electronic distribution curve. The shape of the function near the nuclei still exhibits a considerable amount of the Gaussian character, in that the tangent at the maxima appear to be zero.

Examination of Fig 3 shows some of the nature of the improvement to be expected as one increases the number of basis functions. Although the electronic distribution in the center of the bond is not improved, the character of the function near the nuclei and outside the nuclei, show marked improvements. The two Gaussian functions exhibits a rather flat maximum which is distinctly displaced into the center of the bond (This shift of the maxima was in fact introduced by Gurnee and Magee⁽²⁴⁾ for the hydrogen molecule, who found a displacement of 0.11 a.u toward the center of the molecule). On the other hand the three Gaussian combination displays a rather sharper maxima which is more towards the character of the exact solution. Also it falls off more sharply than the two Gaussian in the region outside the nuclei. One therefore concludes that the improvement in the energy may be attributed to the simultaneous improvement of the function in the immediate region of the nuclei.

With a number of rather drastic assumptions one can attempt an extension of the present results to higher homonuclear diatomic molecules.

If one assumes that the character of the $1s\Delta$ orbital is not much affected by double occupancy or by the presence of electrons in other orbitals, then one may say that the energy of the $1s\Delta$ orbital will vary roughly as the square of the charge on the nuclei. Hence the percentage error introduced by the Gaussian approximation for the $1s\Delta$ orbital will remain roughly constant. The absolute value of this discrepancy will, however, increase. Although this may not have a drastic relative effect upon the total electronic energy, the error so introduced into bond dissociation energy predictions (which remains very roughly constant from molecule to molecule) might be fairly high. From this qualitative argument one might expect that the Gaussian approximation for $1s\Delta$ orbitals in higher molecules may lead to rather large errors in the prediction of bond dissociation energies.

In the application of Gaussians to multi electronic problems, this unfortunate feature may be compensated by the use of a larger number of Gaussian functions per Slater orbital. However there must be made an attempt to limit the number of basis functions so chosen in order to remain within the practical limits imposed by the demands of computation.

Against this unfavorable feature one may set the advantage of Gaussian functions in their application to explicit electronic correlation functions. Further investigation into multi electronic problems are needed to give some indication whether this feature may sufficiently compensate the use of Gaussian functions as compared to Slater orbitals.

Table 1Results from the first trial function: $R = 2 \text{ a.u.}$ *

i	2	3	4	5	6
$E_e \text{ (a.u.)}$	-1.0803	-1.0882	-1.0888	-1.0906	-1.0909
$E_m \text{ (a.u.)}$	-0.5803	-0.5882	-0.5888	-0.5906	-0.5909
m_1	2.0056	0.2803	0.1725	0.1947	0.1392
m_2	0.3343	1.1687	0.6582	0.4666	0.3891
m_3	-	8.1750	0.3014	1.4658	0.9469
m_4	-	-	17.1689	5.5351	2.3044
m_5	-	-	-	34.4770	8.8075
m_6	-	-	-	-	56.9970
C_1	0.1972	0.7429	0.4515	0.3575	0.2209
C_2	0.8653	0.2974	0.5505	0.5207	0.6034
C_3	-	0.0400	0.0848	0.1598	0.1632
C_4	-	-	0.0157	0.0435	0.0887
C_5	-	-	-	0.0068	0.0259
C_6	-	-	-	--	0.0036

* In this and the following tables R indicates internuclear separation, E_e the calculated electronic energy and E_m the calculated molecular energy, i indicates the number of basis functions used.

Table 11Results from the first trial function: $R = 1.8$ and 2.2 a.u.

R (a. u.)	1.8	1.8	2.2	2.2
i	3	6	3	6
E_e (a. u.)	-1.1415	-1.1444	-1.0411	-1.0434
E_m (a. u.)	-0.5860	-0.5888	-0.5865	-0.5889
m_1	0.2857	0.1405	0.2731	0.1392
m_2	1.1687	0.3944	1.1687	0.3893
m_3	8.3420	0.9540	7.9860	0.9438
m_4	-	2.3298	-	2.3052
m_5	-	8.8634	-	8.7666
m_6	-	5.6880	-	56.6568
C_1	0.7088	0.1887	9.7680	0.2425
C_2	0.3312	0.5843	0.2735	0.6041
C_3	0.0411	0.2027	0.0395	0.1306
C_4	-	0.0863	-	0.0914
C_5	-	0.0275	-	0.0241
C_6	-	0.0038	-	0.0036

Table 111

Results from the first trial function: three Gaussian combination

R (a. u.)	10^{-29}	1.9	2.1	20.0
E_e (a. u.)	-1.9702	-1.140	-1.0639	-0.5443
E_m (a. u.)	-1.9702	-0.5877	-0.5877	-0.4943
m_1	0.2970	0.2832	0.2769	0.1883
m_2	1.1687	1.1685	1.1688	1.1681
m_3	0.9413	8.2610	8.0870	9.9291
C_1	0.2753	0.7270	0.7565	0.7930
C_2	0.6626	0.3130	0.2843	0.2946
C_3	0.1991	0.0405	0.0397	0.0291

Table 1V

Value of wave function along internuclear axis

<u>r_A (a.u.)</u>	<u>r_B (a.u.)</u>	<u>$i=2$</u>	<u>$i=3$</u>
1.0	3.0	0.142	0.050
0.3	2.3	0.317	0.330
0.2	2.2	0.338	0.368
0.1	2.1	0.354	0.398
0.0	2.0	0.363	0.412
0.1	1.9	0.365	0.408
0.2	1.8	0.360	0.387
0.3	1.7	0.350	0.355
0.8	1.2	0.278	0.279
0.9	1.1	0.270	0.275
1.0	1.0	0.268	0.274

CHAPTER 1V

THE SECOND TRIAL FUNCTION

The Trial Function:-

One of the classic ways of improving the electronic distribution function in the hydrogen molecular ion problem has been to introduce into the trial function a contribution whose main weight lies along the inter-nuclear axis. Walsh and Matsen⁽⁹⁾, from a one dimensional treatment showed the importance of considering the polarizability of the electron cloud, in fact these workers used a hundred percent constraint to the inter-nuclear axis and obtained a marked improvement in the binding energy. Dickenson introduced the Slater $2p_z$ orbital into the trial function and found an improvement in the energy, along with a satisfactory improvement in the axial distribution curve.

These arguments prompted the choice of the second function

$$\psi = \sum_i C_i N_i \left(e^{-m_i(x_A^2 + y_A^2) - q_i z_A^2} + e^{-m_i(x_B^2 + y_B^2) - q_i z_B^2} \right)$$

Which involves the introduction of a weighting parameter q along the Z -axis, chosen to be the internuclear axis.

Discussion:-

It is recognized that this form is not the most satisfactory, although it is the only one which maintains the simple Gaussian character throughout the trial function along with some aspects of polarization. Its deficiency arises from the impartial character of Z^2 in that the electron distribution along the internuclear axis is affected equally both between and outside the nuclei. This does result in a relative increase in the electron charge density, in the region of the nuclei; but contrary to the

function of Dickenson (and that described in Chapter V) this does not arise from a depletion of electron charge density in the region beyond the nuclei. Rather any building up of charge density in the internuclear region must be effected at the expense of the relative charge density in the region of the nuclei.

That this is not an entirely favorable feature is pointed out by a comparison of the results of this and previous Chapter (using the three Gaussian function as an example). There is a relatively minor effect upon the energy -1.0882 a.u. v_s -1.0894 a.u. for the first and second trial functions respectively. Further one detects a tendency for resistance on the part of the function for any great deviation from spherical character.

In view of the minor improvement in the energy, and of the amount of computation involved in the necessary numerical integration the conclusion is that such an attempt to weight the distribution along the internuclear axis is not recommended.

TABLE VResults from the second trial function: $R = 2$ a. u.

i	2	3	4
E_e (a. u.)	-1.0785	-1.0894	-1.0909
E_m (a. u.)	-0.5785	-0.5894	-0.5909
m_1	2.0056	0.2630	0.1823
m_2	0.3037	1.2177	0.6582
m_3	-	9.5299	2.8858
m_4	-	-	19.1696
q_1	2.0056	0.2997	0.2278
q_2	0.3037	1.0776	0.6582
q_3	-	8.5037	2.8858
q_4	-	-	9.1695
C_1	0.2083	0.7846	0.4769
C_2	0.8082	0.2777	0.5141
C_3	-	0.0435	0.09209
C_4	-	-	0.0147

TABLE VI

Results from the second trial function: three Gaussian combination

R (a.u.)	1.8	2.1	2.2	20
E_e (a.u.)	-1.1424	-1.0631	-1.0414	-0.5362
E_m (a.u.)	-0.5868	-0.5869	-0.5869	-0.4862
m_1	0.2736	0.5453	0.2530	0.2219
m_2	1.2376	2.5561	1.2562	1.3208
m_3	9.1642	23.8021	7.7280	8.5225
q_1	0.2997	0.2997	0.2997	0.2997
q_2	1.1481	1.8496	1.1479	1.1907
q_3	8.5623	5.5674	8.7238	8.6451
C_1	0.1993	0.7990	0.8112	0.8376
C_2	0.5457	0.2655	0.2554	0.2751
C_3	0.2202	0.0431	0.0429	0.0316

CHAPTER V

The Third Trial Function

The Trial Function:-

We had seen in Chapter 111, how the idea of Finkelstein and Horowitz of introducing an effective nuclear charge in the case of the Slater orbitals had served to effect a marked improvement in the energy, one of the reasons being the presence of a larger nuclear charge, resulting in a greater attraction for the electron, causing thereby an increased electronic concentration in the internuclear region. Following these lines of argument, and the work of Walsh and Matsen, we tried the second type of function with the idea of weighting along the Z axis, chosen to be the co-ordinate along which the internuclear axis lies. However this resulted in an increase of the electronic density in the middle of the two nuclei, at the expense of that in nuclear regions.

Dickenson improved upon the Finkelstein - Horowitz result by the introduction of a 2p orbital. This orbital when centered upon the nuclei would make a negative contribution towards the electronic cloud in the outer regions, and a positive contribution in between the two nuclei. The introduction of this p orbital did in fact markedly improve the energy. Following this method of Dickenson we used a function of the following form:

$$N C (e^{-m_1 r_A} e^{-m_1 r_B}) + N_2 C_2 (e^{-m_2 r_A} e^{-m_2 r_B}) + N_Z C_Z (r_A \cos \theta_A e^{-a r_A^2} + r_B \cos \theta_B e^{-a r_B^2})$$

which in effect is a linear combination of two s type functions and one p type function, centered at each nucleus.

Discussion:-

At an internuclear separation of two atomic units a molecular energy of -0.5878 a.u. was obtained, as against values of -0.5803 a.u. and -0.5882 a.u. from linear combination of two and three s type Gaussian functions respectively.

This alone suggest that with the restricted practical basis set used the problem is not necessarily that of increasing the electron distribution in the internuclear region but an improvement over the entire molecule, including the region at the nuclei.

An examination of the results given in Tables VIII and figures 3 and 4 shows that there is minimal improvement in the electronic distribution over the whole molecule as one increases the basis set from two s type Gaussian functions to the combination of the latter and one p type function. It is indeed more favorable to use s type function as a third member of the basis set.

This result does not parallel that of Dickenson who found an improvement of 0.0175 a.u. in the energy. The prime difference between the basis set used by Dickenson and that used here is the Gaussian form of the latter. In both cases, however, the approximate contribution of the p type wave function is under 5%. This would seem to indicate that the expected effect of the p type function is being offset by the fact that the small number of s type Gaussian functions used do not accurately describe the distribution near the nuclei. A 1s Slater function properly describes

certain of the characters of the exact function in this region, in particular the discontinuities in the tangent at the nuclei. The results given in Chapter III show that these characteristics can be approached by increasing the number of s type functions in the basis set. The conclusion to be drawn from the above results are that such an increase is necessary before one can expect an independent improvement by the introduction of a p type function. An enlarged basis set would however, imply evaluation of a very large number of matrix elements and of individual energies for an optimization. The amount of computation required for both of these portions depends approximately on the second power of the number of functions in the basis set.

From a practical point of view one may say that the application of Gaussian functions to molecular orbital calculations is limited by the availability of high speed computers of large capacity. This conclusion however does not exclude the possible use of a small basis set of Gaussian functions in problems involving the explicit use of inter electronic coordinates where Slater functions introduce rather formidable integrals.

Table V11

Results from third trial function: Linear combination of three Gaussian functions

R a. u.	1.8	2.0	2.2	2.4
E_e	-1.1401	-1.0878	-1.0417	-1.0023
E_m	-0.5845	-0.5878	-0.5871	-0.5857
m_1	2.3342	2.1342	2.3046	2.3915
m_2	0.3831	0.3471	0.3471	0.3486
q_3	0.08002	0.1001	0.0790	0.0791
C_1	0.1234	0.1296	0.1165	0.1097
C_2	0.4643	0.4653	0.4859	0.5001
C_7	0.1257	0.1086	0.1201	0.1225

Table V111

Value of function along internuclear axis.

r_A	r_B	s contribution	p contribution	Total ψ functions
1.0	2.0	0.1313	0.0027	0.1340
0.3	1.3	0.3027	0.0092	0.3119
0.2	1.2	0.3244	0.0101	0.3345
0.1	2.1	0.3402	0.0109	0.3511
0.0	1.0	0.3492	0.0117	0.3609
0.1	0.9	0.3507	0.0124	0.3631
0.2	0.8	0.3454	0.0131	0.3585
0.3	0.7	0.3341	0.0137	0.3478
0.8	0.2	0.2594	0.0156	0.2750
0.9	0.1	0.2538	0.0157	0.2695
1.0	0.0	0.2535	0.0158	0.2693

Table 1X

Comparison of energy at internuclear distance of 2 a. u.

Burrau	-0.5987
Hyelleraas	-0.5993
Jaffe	-0.5993
Guillimin and Zener	-0.5992
Finkelstein and Horowitz	-0.5799
Dickenson	-0.5976

Present work:-

First trial function

$i = 2$	-0.5803
$i = 3$	-0.5882
$i = 4$	-0.5888
$i = 5$	-0.5906
$i = 6$	-0.5904

Second trial function

$i = 2$	-0.5785
$i = 3$	-0.5899
$i = 4$	-0.5909

Third trial function

$i = 3$	-0.5878
---------	---------

Chapter VI

Spectroscopic Constants

In Table ~~X~~ are collected the data used in calculating the various spectroscopic constants. The constants are displayed in Table ~~XI~~
 The formulae used in this calculation were taken from a publication by Fraga
 (25)
 and Ransil .

The majority of the results are surprisingly good considering the comments which have been made in the preceding Chapter. Fraga and Ransil from a study of a wide variety of diatomic molecules conclude "The rather regular behavior suggests the possibility of ω_e and $\omega_e x_e$ as criteria for the "goodness" of a wave function". although they detect no correlation between the accuracy of these quantities and that of the calculated total energies or dissociation energies.

The present results, coupled with the information obtained on the actual values of the wave function, cast severe doubt upon any safe prediction of the goodness of the wave function based on derived spectroscopic constants. In this regard it may be reported that a preliminary investigation using an assuredly absurd wave function gave rise to spectroscopic constants which were as good as or better than reported by Fraga and Ransil.

Table X

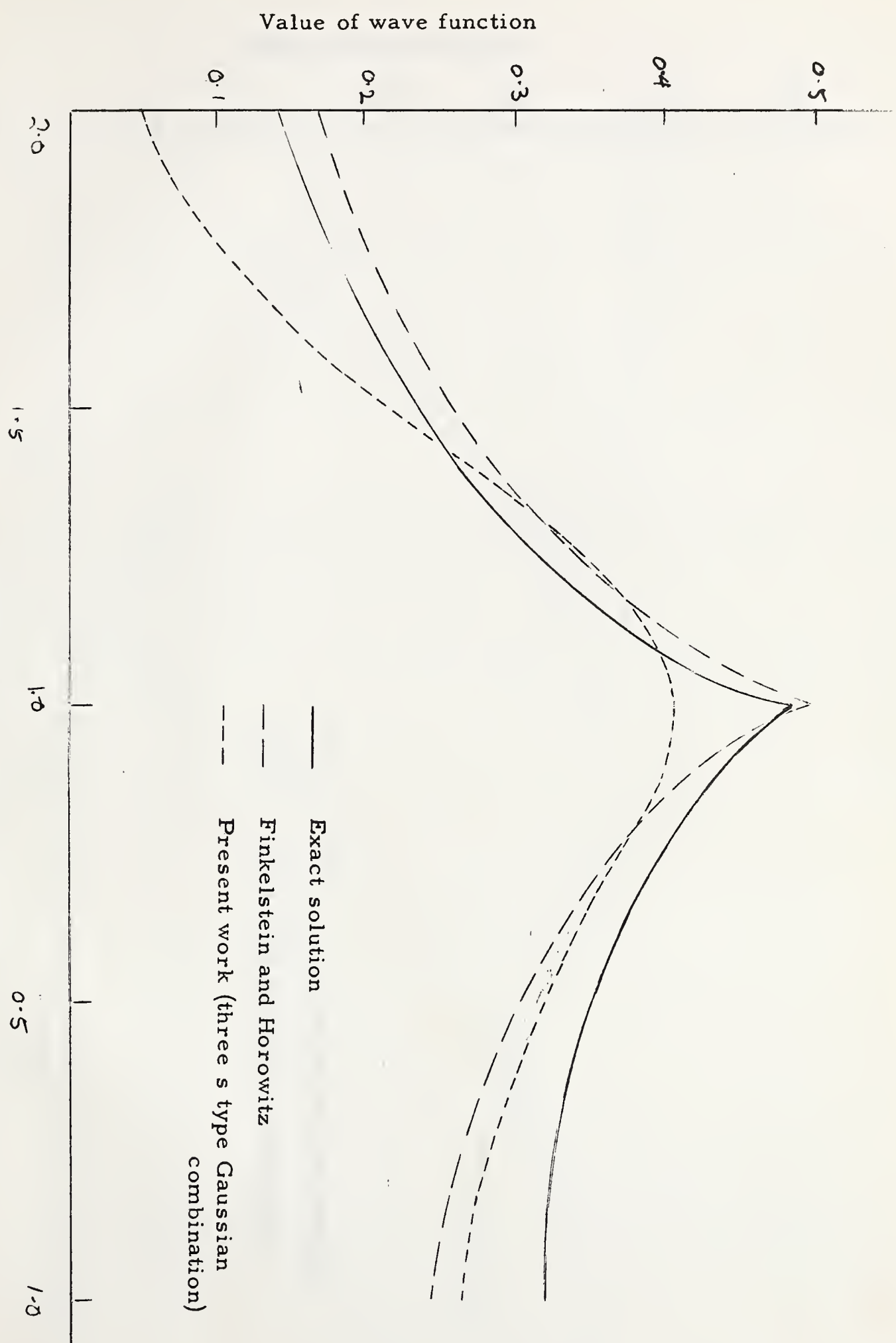
Data used in calculation of spectroscopic constants

<u>First function</u>		<u>Third function</u>	
R = 1.8	E _m = -0.58597	R = 1.8	E _m = -0.58454
1.9	= -0.58771	2.0	= -0.58776
2.0	= -0.58821	2.2	= -0.58715
2.1	= -0.58775	2.4	= -0.58570

Table XI

Spectroscopic Constants

	$\omega_e(\text{cm}^{-1})$	$\omega_{ex_e}(\text{cm}^{-1})$	$\text{Be}(\text{cm}^{-1})$	$\alpha_e(\text{cm}^{-1})$	$\text{Re}(\text{\AA}^0)$	$E_m(\text{a.u.})$	$10^{-5}k_e(\text{dynes/cm})$
First function	2249	197	30.0	2.1	1.057	-0.5882	1.501
Third function	2024	554	28.5	5.4	1.083	-0.5879	1.216
Fraga and Ransil ⁽²⁵⁾	2275	227	28.0	2.2	1.093	-0.5791	1.536
Experimental	2297	62	29.8	1.4	1.06	-0.6026	1.566



Distance from the center of bond (a.u.)

Fig. 2: Axial plot of wave function

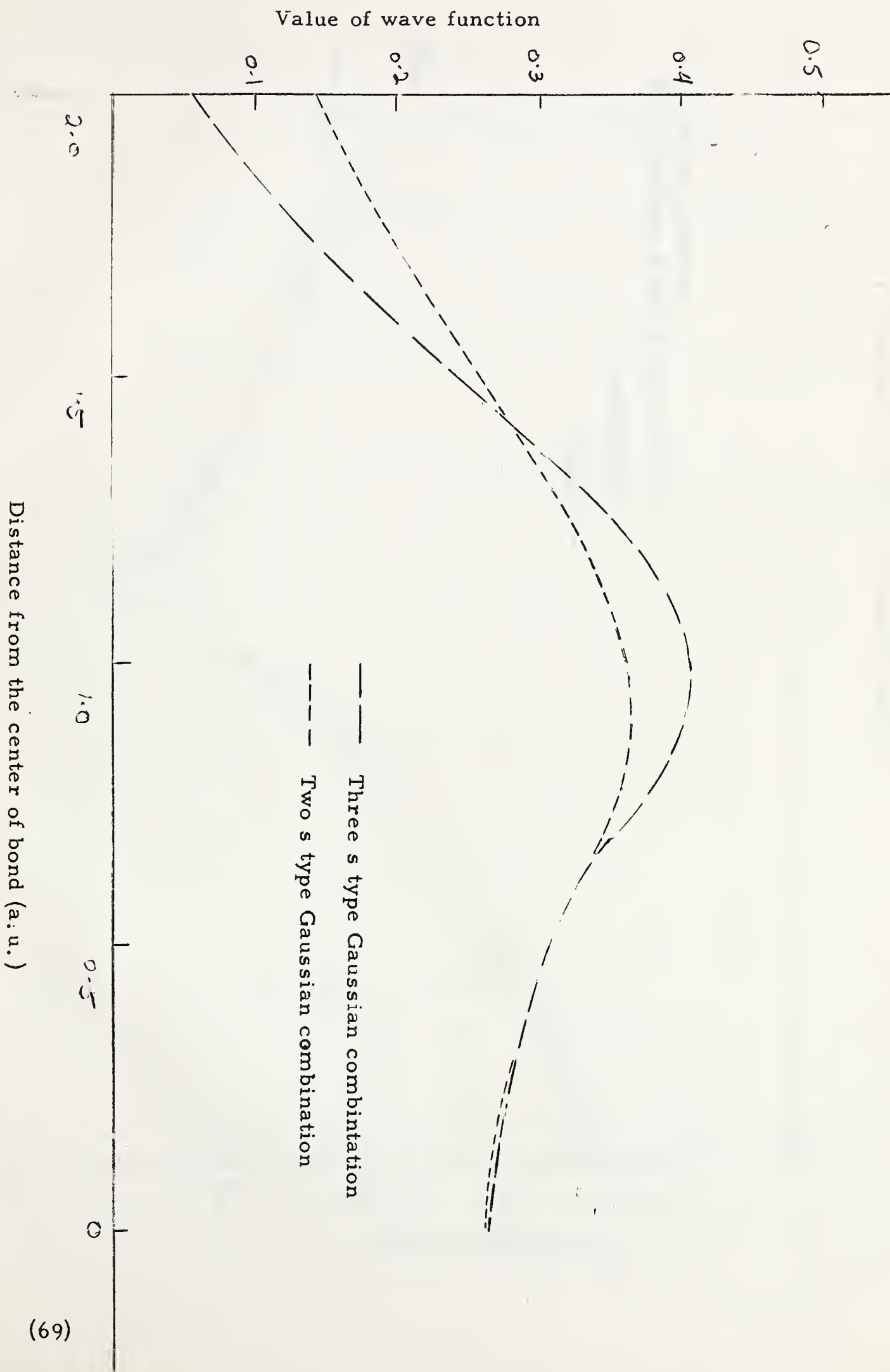
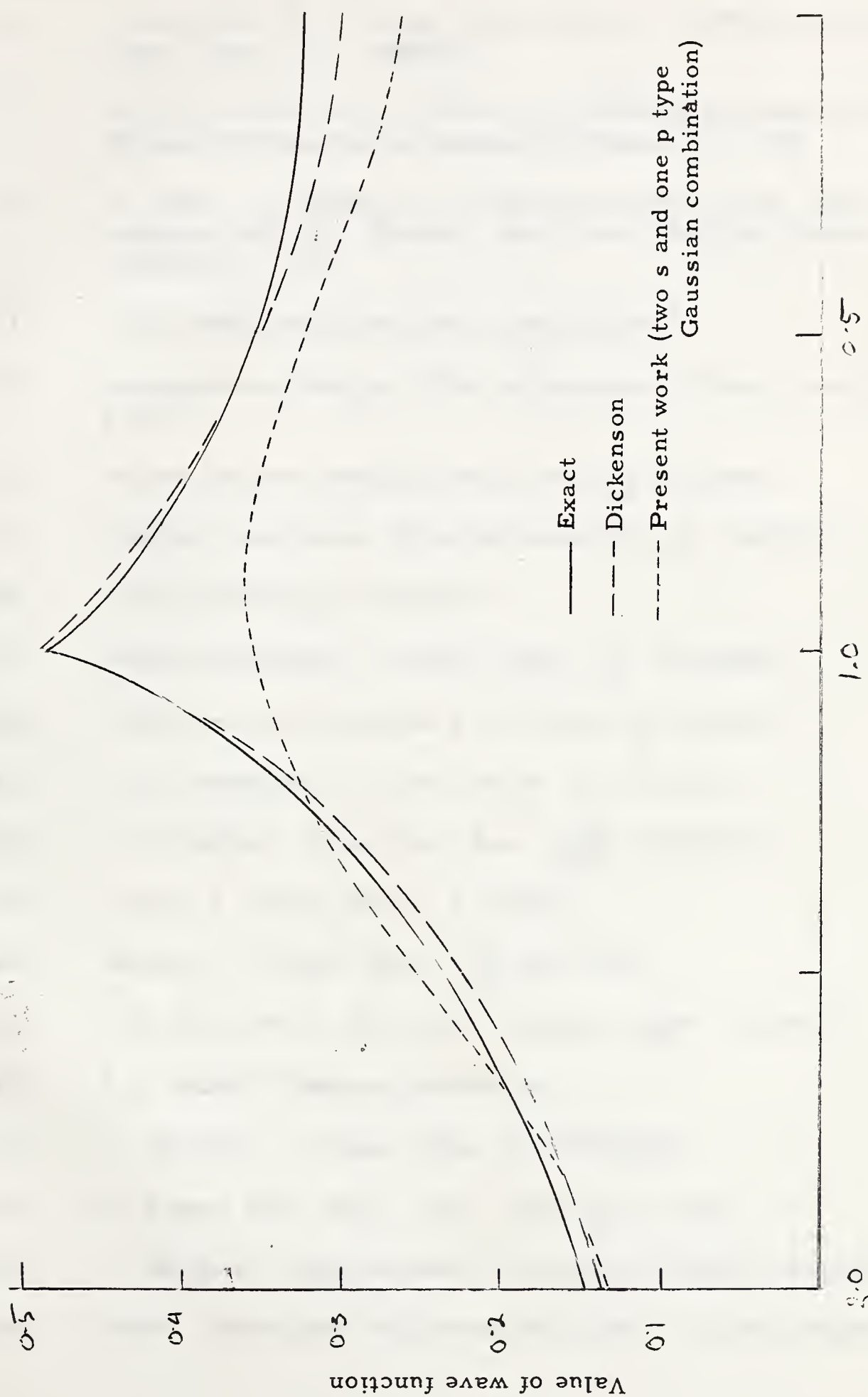


Fig. 3: Axial plot of the wave function



Distance from the center of bond (a.u.)

Fig. 4: Axial plot of the wave function.

BIBLIOGRAPHY:-

- (1) Burrau Det. Kgl. Danske Vid. Selskab. 1 1(1927), see also Pauling Chem. Revs. 5 183(1923)
- (2) E.A. Hylleraas Z. f. Phys. 71 739(1931), see also Pauling and Wilson "Introduction to Quantum Mechanics" p. 338
- (3) G. Jaffe Z. f. Phys. 87 535 (1934), see also D.R. Bates, K. Ledsham and A.L. Stewart, Phil Trans. Roy Soc. London A246 215(1953)
- (4) S.K. Chakravarty Phil. Mag. 28 423(1939)
- (5) Margenau and Murphy "The Mathematics of Physics and Chemistry" p. 107
- (6) Morse and Stueckelberg Phys. Rev. 33 932(1929)
- (7) Guillemin and Zener Proc Nat Acad. Sci. 15 314(1929)
- (8) Unsöld Physik 43 583(1927)
- (9) Walsh and Matsen J. Chem. Phys. 17 1343(1949)
- (10) Finkelstein and Horowitz Z.f. Phys. 48 118(1928)
- (11) B.N. Dickenson J. Chem. Phys. 1 317(1933)
- (12) A.C. Hurley. Proc. Roy. Soc. A226 179(1954)
- (13) James J. Chem. Phys. 3 9(1935)
- (14) Matsen J. Chem. Phys. 27 928 (1953)
- (15) S.A. Boys Proc. Roy. Soc. (London) A200 542(1950)
- (16) L.I. Schiff "Quantum Mechanics"
- (17) A. Meckler J. Chem. Phys. 21 1750(1953)
- (18) B. Ransil Rev. Mod. Phys. 239 32 (1960)
- (19) C. Hastings "Approximation methods for digital computers"
- (20) Dirac "Principals of Quantum Mechanics" Fourth edition p. 18

- (21) Hartree "Numerical Analysis" pp. 120-122
- (22) Kauzman "Quantum Chemistry" p. 230
- (23) Longstaff and Singer Proc. Roy. Soc. A258 421
- (24) Gurnee and Magee J. Chem. Phys. 1 317(1933)
- (25) Fraga and Ransil J. Chem. Phys. : 35 669 (1961)

B29802